PROCEEDINGS ◆ COMPTES-RENDUS

5th / 5ième

Technical Seminar on Chemical Spills

Colloque technique sur le déversement de produits chimiques

February 9-11, 1988
Montréal, Québec

9 au 11 février 1988
Montréal, Québec

Environment Canada
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Canada

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Seminar sponsored by

Technology Development and
Technical Services Branch
Environmental Protection
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Colloque commanité par

Direction du développement
technologique et des services
techniques
Protection de l'environnement
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BOILING LIQUID EXPANDING VAPOUR EXPLOSIONS - AN UPDATE

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ABSTRACT

BLEVEs (*B*oiling *L*iquid *E*xpanding *V*apour *E*xplosions) can occur when a pressure liquified gas tank is in a fire. Vessel contents are at a temperature above their atmospheric boiling point. When the tank ruptures there is flash evaporation. Energy is released quickly and an explosion results. Research is being done on BLEVEs with propane and Freon 12 at the University of New Brunswick.

The theory that the superheat temperature is the minimum temperature necessary for a BLEVE is discussed (and disproved), and the relationship between temperature, pressure and volume as they relate to internal energy is shown. The suggestion that a fireball is necessary for an incident to be classed as a BLEVE is shown to be wrong. The relationship between detonation wave theory and results with BLEVEs is discussed.

INTRODUCTION

A BLEVE is defined as a major container failure, into two or more pieces, at a moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure.[1] A typical example is that of a propane tank engulfed in a fire.

As the fire heats the liquified gas, the pressure inside the container increases. The temperature of the tank metal below the liquid level does not rise much above the boiling point of the contained fluid because the heat added by the fire is removed by the boiling propane. However, the metal above the liquid level increases in temperature since heat transfer between the metal and the vapour is relatively poor. When the pressure inside the tank reaches the set pressure of the safety relief valve, the valve opens to keep the tank at this pressure. While this pressure would be safe at normal temperatures, the metal is now weakened by the high temperature due to the fire. This metal fails and the fluid is open to atmospheric pressure. Since propane is a gas at atmospheric pressure, rapid boiling begins and there is an explosion.

Once containment is lost, the liquid inside the tank boils since it is no longer under pressure, and gives the first two letters of the phenomenon - *B*oiling *L*iquid. As the liquid boils, vapour is formed. The specific volume of the vapour is much larger than that of the liquid, so there is expansion - *E*xpanding *V*apour. There is an *E*xplosion because there is a shock wave and the container is torn apart.

But under what conditions do tanks and their contents BLEVE? Not every pressurized liquid container BLEVEs when a tear develops in a tank. What is special about the vessels that have BLEVEd? And what can be done to tank design to minimize the occurrence of this type of explosion?

[1] Walls, WL, "The BLEVE - Part 1", Fire Command, p24, May, 1979

BLEVE EXPERIMENTS

Since a BLEVE is an explosion due to rapid boiling, there is no ignition or chemical reaction involved. To absolutely prove this, experiments have been done with both propane (a common fluid involved in large scale, very damaging BLEVEs) and a noncombustible fluid, Freon 12 (R12). The tanks used were commercially available 1 ℓ propane cylinders (see Figure 1).

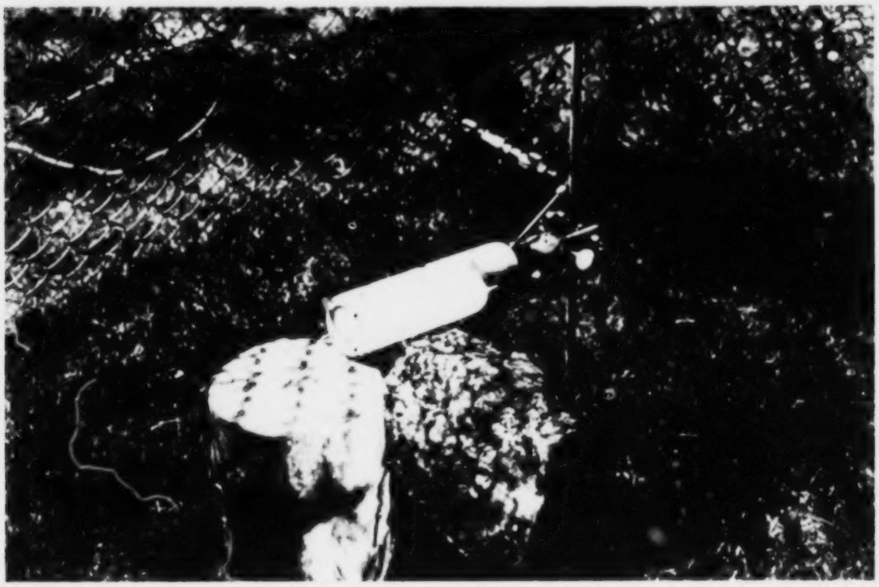

Figure 1: Instrumented experimental tanks

The relief valve was removed from these tanks and they were purged with nitrogen. The instrument cluster of 3 type T thermocouples and a 0 - 1000 psig Mediamate pressure transducer was inserted in the hole left by the valve. The cylinders were then placed in a -45 deg C temperature bath and filled to the desired weight with propane or R12. The filled, instrumented cylinders were then ready to test.

Most experiments were carried out at the Lake George Gun Club, 40 km from Fredericton. The cylinders were mounted horizontally about 0.6 m above the ground and a propane torch was placed so that the flame would impinge on the bottom of the cylinder (see Figure 2). This simulates a normal BLEVE situation; there is either total fire engulfment or flame impingement on the tank. The instrumentation was connected to a Hewlett-Packard 3497A Data Acquisition Unit, driven by an HP 85 computer. The computer recorded and printed temperature and pressure information. A high speed camera was set up with a remote trigger to record the event at a maximum of 10 000 pictures per second (pps) (see Figure 3). A remote digital thermometer and the camera trigger were mounted in the club house, 75 m from the cylinder. A chain link fence enclosure was placed around the cylinder to contain the flying pieces

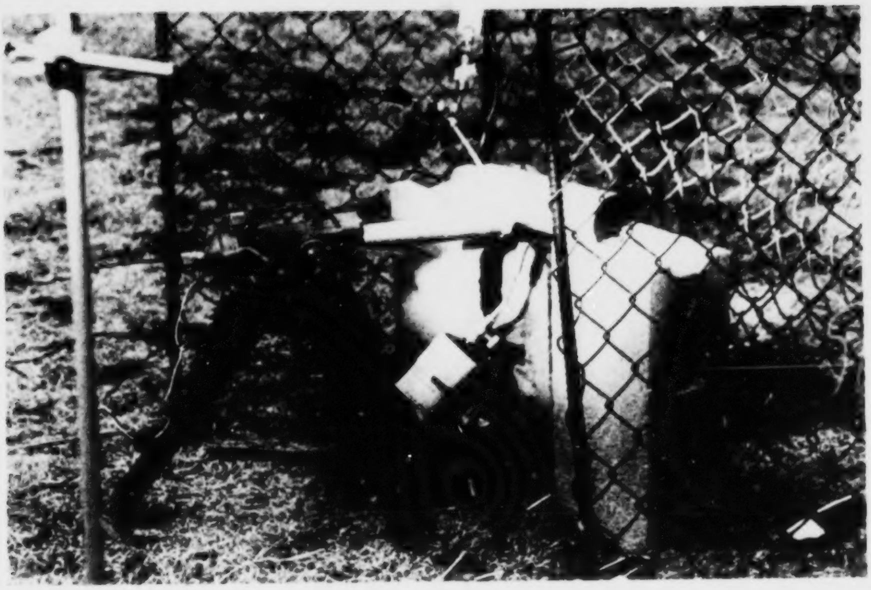

Figure 2: Tank with propane torch as heating element

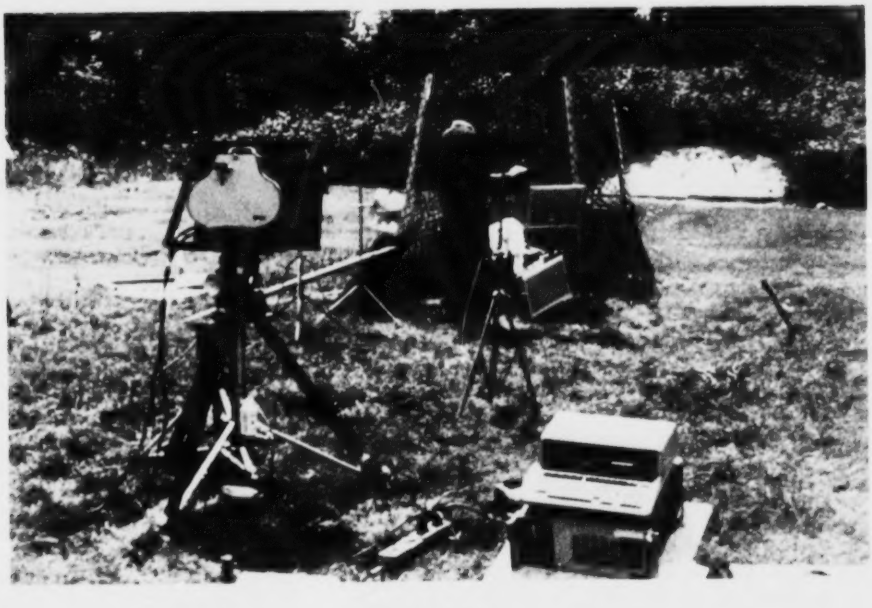

Figure 3: Experimental set-up; tank, computer and camera

of the tank and to protect equipment and personnel.

In a BLEVE, the tank metal tears and opens the contents to atmospheric pressure. For research, however, it is necessary to open the tank when it reaches a given set of internal conditions. For example, if the purpose is to see if a certain tank will BLEVE at 55 deg C, the tank must be punctured at that temperature; it cannot be left to fail on its own. A .22-250 rifle with full metal jacketed bullets was used to rupture the tank at the desired temperature. Later a series of tests were carried out with a water gun provided and manned by J division of the RCMP. This gun shoots a 100 ml slug of water (2 cm diameter) at a maximum velocity of 189 m/sec to a maximum pressure of 124 000 kPa. (See Figure 4)

Once the instrumentation was connected and tested, the torch under the cylinder was lit and all personnel moved into the club house to watch the temperature rise on the remote thermometer. When the bulk temperature reached the test value, the camera was started and the rifle fired. Results (BLEVE / no BLEVE) were recorded and the pieces photographed (see Figure 5).

Before the water gun was used, it was first tested on an empty cylinder and one filled with water to ensure that it could penetrate the tank wall. Once this was proven, it was used in the same manner as the rifle.

BLEVE / no BLEVE

Results of 1 ℓ cylinders with propane and R12 contents are presented in Table 1. Tests 3 - 36 are an attempt to determine the relationship between temperature and BLEVEs - to actually test the theory that the minimum temperature below which no BLEVE can occur is the superheat temperature limit (T_{sl}). (For more information on this theory, see McDevitt et al, 1987). This temperature is 53 deg C for propane and 69 deg C for R12.

Cylinders were heated to a specific temperature and then ruptured. The purpose was to test whether a BLEVE would occur below the T_{sl}. Not all cylinders used for these tests contained the same weight of fluid. Results showed that one factor which determines whether a tank BLEVEs is the amount of fluid. For example, Tank 12 had 434 g of propane and BLEVEd at 55 deg C; Tank 16, with only 329 g did not explode at 57 deg C, nor did Tank 34 at 65 deg C (252 g propane). Temperature, then, could not be the only important parameter. If it were, tanks 16 and 34 should have exploded since they were above T_{sl}.

The quantity Q has been defined as the amount of heat that would be released when the liquid changes from its pressurized condition in the tank to saturated liquid at atmospheric pressure (Osigo, 1972). Q is calculated from the equation

$$Q = g\ (H_2 - H_o)$$

where Q is in kJoules, g is the weight of the fluid in grams, H_2 is the liquid enthalpy of the fluid at the time of rupture and H_o is the enthalpy of the saturated liquid at its normal boiling point, both in J/g. Q is the heat initially available to vapourize the fluid. Thus Q is a measure of the amount of vapour that will be formed. No cylinders BLEVEd below a Q of 96.7 kJ, while all of the tanks with a Q above this value did BLEVE.

The next series, numbers 41 - 47, attempt to test the possibility that the occurance of a BLEVE depends on the amount of vapour that could be produced when the tank was ruptured. With the minimum Q now known, results

Figure 4: Set-up with water gun

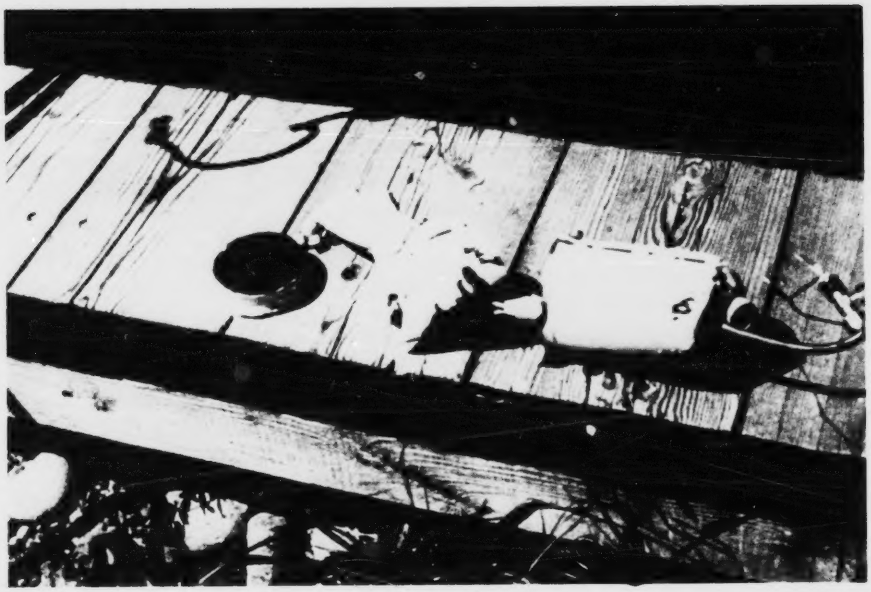

Figure 5: Cylinder which has BLEVEd

TABLE 1: BLEVE RESEARCH RESULTS

TEST	FLUID	T_{max} deg C	P kPag	WEIGHT g	H_2 J/g	Q kJ	RESULT
* 3	Propane	12	-	130	125.530	16.936	-
5	Propane	16	-	~138	135.957	~19.417	-
* 6	Propane	64	-	154	274.449	42.996	-
* 7	Propane	101	-	125	-	-	-
8	Propane	82	6143	501	339.373	172.403	BLEVE
11	Propane	65	2696	369	277.790	104.255	BLEVE
12	Propane	55	2200	434	245.767	108.722	BLEVE
E	Propane	35	1331	~340	187.180	~65.255	-
4	Propane	86	3930	384	356.960	138.895	BLEVE
14	Propane	73	3034	368	305.401	114.134	BLEVE
15	Propane	56	1979	332	248.866	84.199	-
16	Propane	57	2241	329	251.962	84.457	-
18	R12	73	-	1136.9	110.813	115.757	BLEVE
21	R12	39	2082	914.2	73.575	59.039	-
22	R12	71	2310	938.5	108.468	93.355	-
23	Propane	61	2613	419	264.657	112.879	BLEVE
31	Propane	58	2179	319	255.099	82.890	-
32	Propane	56	2413	340	248.866	86.228	-
33	Propane	56	2268	355	248.866	90.032	-
*34	Propane	72	2820	252	277.790	73.167	-
*35	Propane	60	2337	331	261.468	88.117	-
36	Propane	70	3358	323	294.774	96.745	BLEVE
41	Propane	50	-	430	230.349	101.090	BLEVE
*42	Propane	52.6	-	424	239.715	103.651	-
43	Propane	65	-	448	277.790	126.576	BLEVE
44	R12	66	-	1082	102.614	101.296	BLEVE
45	R12	67	3744	1133	103.761	107.030	BLEVE
46	R12	67	3013	1112	103.761	105.380	BLEVE
47	R12	59	2082	1131	94.650	96.876	BLEVE

H values from ASHRAE Handbook, 1981 Fundamentals (Basis: H_0 = 0 for sat liq propane at -45 deg C, sat liq R12 at -40 deg C)

* Only 1 thermocouple working, may be vapour temperature

could be predicted. Calculations based on the minimum Q of 96.7 kJ show that a cylinder should BLEVE at 50 deg C if it contains at least 427 g of propane and at 65 deg C with at least 1077 g R12. Both of these temperatures are below the T_{sl}, so if these tanks explode then BLEVEs can occur below that temperature. Cylinder 41 was filled with 430 g of propane and burst at 50 deg C - it BLEVEd, as predicted. Tank 44 which had an R12 lading of 1082 g also BLEVEd below its T_{sl}, at 66 deg C.

Tanks 45, 46 and 47 were filled with 1133, 1112, and 1131 g of R12, respectively. All of these tanks were predicted to BLEVE at 65 deg C or higher. The water gun was used by the RCMP to rupture these cylinders.

Tank 46 was burst at 67 deg C and BLEVEd. The gun was aimed at the liquid space, as in most of the previous tests. To determine if rupture location had any bearing on the results, the gun was suspended above the cylinders and aimed at the top (vapour space) for the next two tests. Both of these tanks BLEVEd, tank 45 at 67 deg C and tank 47 at 59 deg C.

The temperatures quoted so far are bulk liquid temperatures, measured near the bottom of the tank. There is some stratification in the liquid, and the vapour temperature is also higher than the liquid temperature. Typically the spread in propane tanks is 2 deg C to a maximum of 6 deg C, and 11 deg C for R12 tanks. Because these cylinders are more than 90% liquid full at rupture conditions, the vapour temperature is not really significant. For test 47 the liquid bulk temperature was 59 deg C and the vapour temperature was 68 deg C. Thus all temperatures in the vessel were below the T_{sl} of 69 deg C. Based on these tests, it is possible to have a BLEVE below that temperature. The superheat temperature limit therefore cannot be used to predict a BLEVE.

To ensure that the temperature measurement was accurate, all of the thermocouples in the last three tests were calibrated at room temperature and in boiling water and shown to be accurate to ± 0.3 deg C. To check response time, they were heated with a match and immersed in cold water while temperature vs time was plotted. The plots showed that the thermocouples responded much faster than the temperature of the fluid in the cylinders changed.

DISCUSSION

Follow the progression of a BLEVE in Figures 6 and 7. First the bullet passes through the cylinder (a), making the same size hole on both entry and exit. There is tearing from the exit hole longitudinally until the tear encounters the welded, double metal of the center and bottom seams. Then the tears progress circumferentially in both directions, opening up and flattening out the lower section of the cylinder (b). As the tears progress to the front of the tank, the ends of the cylinders begin to move away from each other (c). The bottom half of the tank becomes completely separated from the top, the top half moves to the right, the bottom to the left and the flattened piece is projected toward the camera (d). Note that figure 6 is a propane BLEVE and figure 7 has R12 as the fluid. The mechanism and results are identical in both cases.

Parameters

Logically, it takes a certain amount of energy released to do the type of damage seen in the figures. If this much energy is not available, then the tank will not BLEVE. Q, a measure of the amount of vapour produced, is also

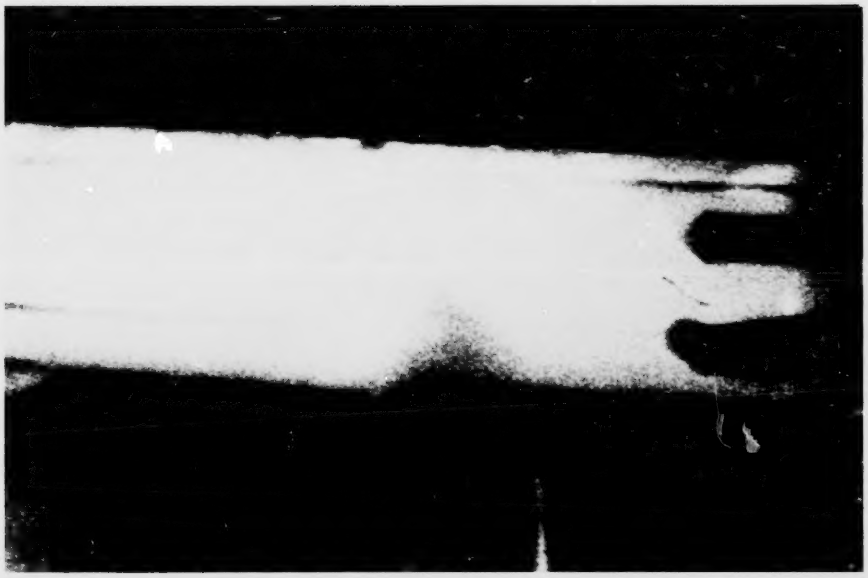

Figure 6: Propane BLEVE at 73 deg C. (a) at rupture

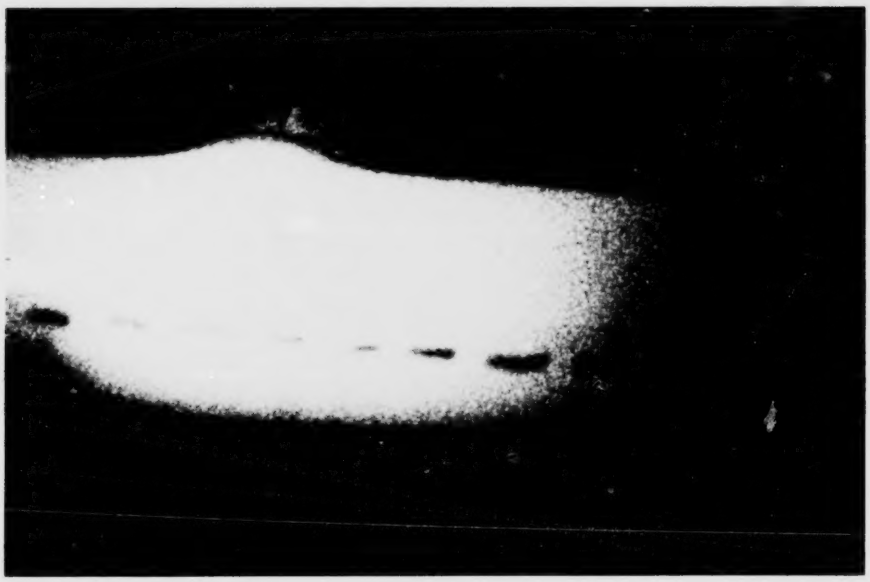

Figure 7: R12 BLEVE at 73 deg C. (a) at rupture

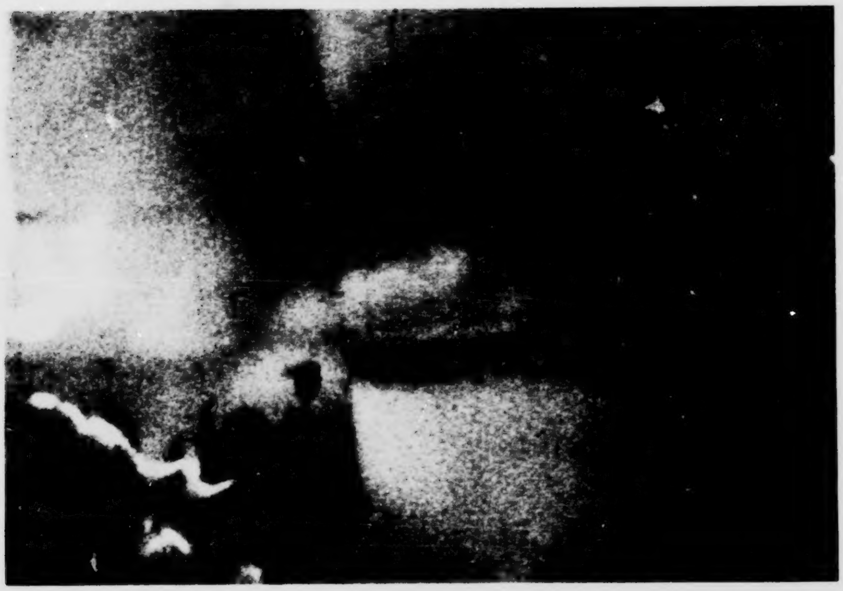

Figure 6 (b): after 1 ms

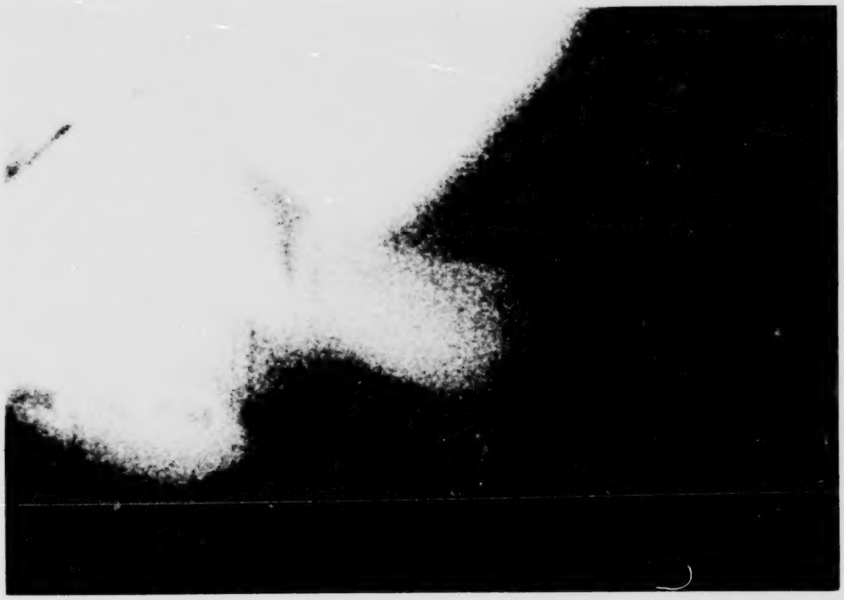

Figure 7 (b) after 1.25 ms

Figure 6 (c) after 1.5 ms

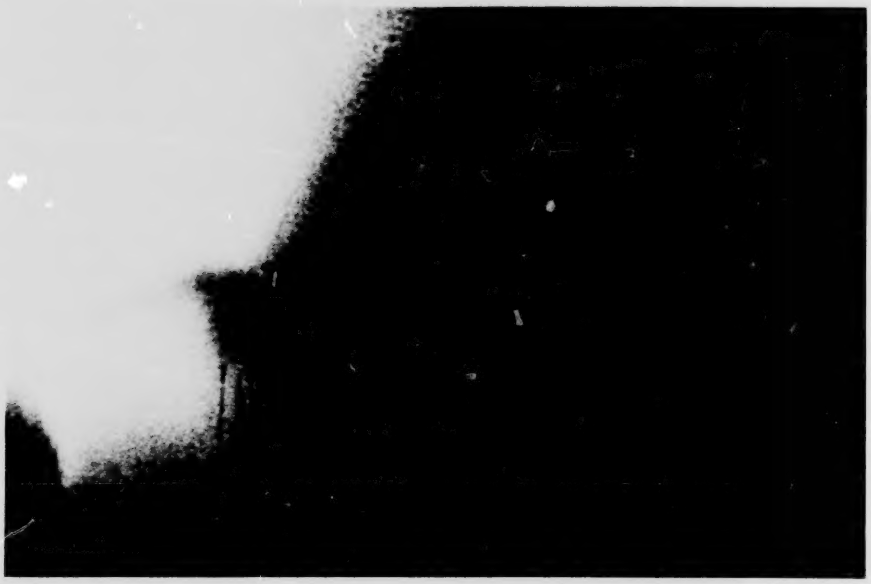

Figure 7 (c) after 2.5 ms

Figure 6 (d) after 2 ms

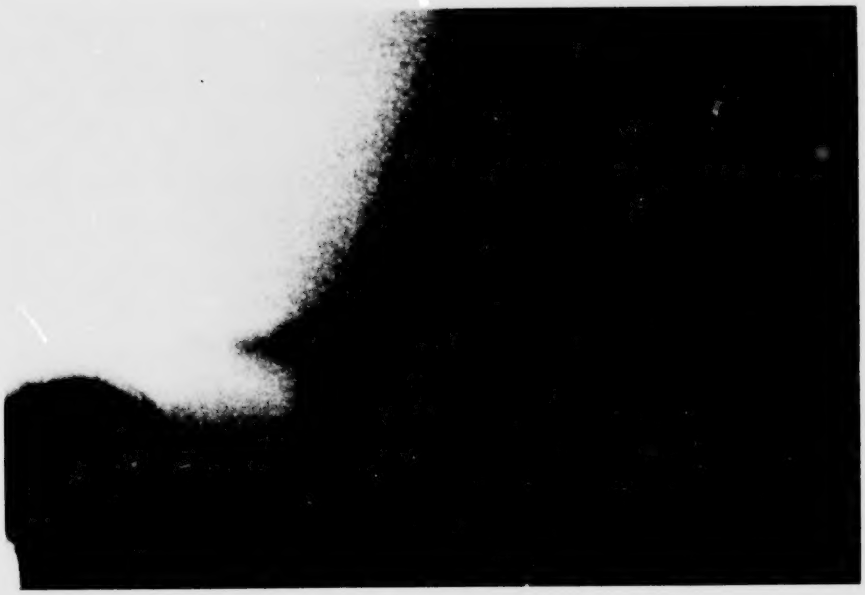

Figure 7 (d) after 2.75 ms

a measure of the destructive energy available. For these particular cylinders, assuming constant conversion of energy to destructive work, Q must be above 96.7 kJoules. If the cylinder were of a different metal, with different yield stress, then the required Q could be different. This assumes that it is the vapourization that is driving the explosion.

Waves

Another phenomenon, previously unmentioned, is that of sonic waves. When the hole is made in the tank, the surrounding fluid sees atmospheric pressure. This new pressure information must be transmitted to the rest of the fluid. Therefore there must be a rarefaction wave which travels at the speed of sound in the liquid. Just behind this wave there will be boiling fluid, which will cause pressurization, thus a pressure wave will follow the rarefaction wave. The pressure wave may be slower because it is not travelling through a homogeneous liquid, but through a two-phase mixture. These two waves have not been seen or measured, but they may have some effect on the events during the explosion.

Fireballs

Finally, the issue of the fireball. When a propane tank BLEVEs, it leaves a large propane vapour cloud. If there is some source of ignition, usually the fire which caused the BLEVE, then this cloud can ignite and a fireball may form. These fireballs can be a hundred metres in diameter, and are quite spectacular. They also cause more damage than the explosion. Most papers published from the scientific community recognize that the BLEVE and the fireball are two separate events and not really related. There is overpressure associated with a BLEVE, and none with a fireball. The only real relationship is that the BLEVE provides fuel for the fireball.

There are some authors in industry, however, who suggest that the definition of a BLEVE be changed to include the fireball. They suggest that if there is no fireball, there is no explosion (Lewis, 1985; Ens, 1985). Our research has shown that the two events are most definitely separate, one occurring much later than the other. Results show the explosion and 260 ms later, after all of the pieces of the container are beyond the field of view of the camera, the ignition of the vapour and a fireball. In fact most of our BLEVEs, even with propane, had no fireball as there was no source of ignition. It is important for firefighters, loss prevention and risk analysis personnel to recognize the BLEVE potential even when dealing with inerts.

THEORIES

Detonation

There are some similarities between a boiling liquid explosion and a detonation (chemical reaction-driven explosion). The most obvious is that they are both explosions, ie both produce overpressures and make a loud noise (the wave is supersonic). It is possible that the similarities go further.

Detonation is in itself a process in which there is much uncertainty and much research. However a rough description of how a detonation proceeds is as follows:

> A shock wave propagating into undisturbed explosive material instantaneously compresses and heats it enough to initiate chemical reactions that, over the course of several nanoseconds, release energy. The energy in turn preserves the conditions of high pressure and temperature necessary to drive the shock wave forward. When the reactions have run to completion at the end of the reaction zone, the gases expand to do work.[2]

In the case of a BLEVE, the shock wave would be the rarefaction wave carrying the new pressure information to the fluid, at the sonic velocity. In its wake will be a pressure wave due to the boiling of the fluid as it sees atmospheric pressure. This wave will be slower and broader because it is travelling through a two-phase mixture and the speed of sound in vapour is much slower. There would be pressurization due to the limited volume. The gas expansion does work, the work of tearing the cylinder.

A possible scenario which fits the observations to date is as follows: The cylinder is partially opened by the bullet and the rarefaction wave begins at the hole and travels toward the ends of the tank. In its wake it leaves boiling fluid. This fluid cannot continue to boil because as the pressure is raised (due to vapourization), boiling will stop. There will be bubble colapse in this region, which is known to cause large pressure rises. This starts to tear the center section of the tank. As the rarefaction wave hits the ends of the cylinders, a large ΔP occurs which causes the ends of the tank to move away from each other. The center section is already torn open, and the movement of the end sections continues this tearing. Boiling will start at the end sections, giving the rocketing effect, but there is no damage here as there is no bubble colapse. (There is nothing to sustain pressure on the fluid as the container is now fully open to the atmosphere).

FUTURE WORK

There must be rarefaction and pressure waves propagating through the fluid, but these have not as yet been measured. It may be the pressurization due to the boiling which is causing the explosion, as mentioned above. There also will be bubble collapse associated with this pressurization, and that occurrence is also known to produce overpressures. The next step in this research is to try and see what is going on inside the cylinder just as there is a tear.

This will probably be done in a typical shock tube, modified so that there are blow-out sections and a section that can easily be punctured. Then high speed filming will hopefully show the boiling, and rapid recording instrumentation will mark the wave travel. With this type of set up, and a view inside the tank, perhaps there will quantifications of BLEVE phenominom.

CONCLUSIONS

The superheat temperature limit cannot be used to predict BLEVEs. It has been shown that BLEVEs can occur below this temperature. There is a relationship between fluid temperature, fluid volume and the energy required to drive the BLEVE. For 1 ℓ commercial propane cylinders, Q must be above 96.7 kJoules for the experiments conducted.

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[2] Davis, WC, "The Detonation of Explosives", Scientific American, May 1987

Fireballs occur after the BLEVE. They are not part of the tank destruction. There can be a BLEVE without a fireball just as there can be fireballs without any boiling liquid.

Experiments should be conducted in a windowed shock tube. These experiments should give information concerning the mechanism inside the tank.

Rupture location (vapour vs liquid space) appears to have no effect on whether a container will BLEVE.

ACKNOWLEDGEMENT

The authors would like to express their thanks to J Division of the RCMP, and in particular Special Constable H Gould, for their cooperation and assistance.

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SPILLS OF CHEMICALS INTO RIVERS

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ABSTRACT

A computer program has been developed to assess the impact that a spilled chemical will have on the water quality at any point downstream of the accident.

INTRODUCTION

The amount of chemicals shipped in the United States by barge will roughly double by the year 2000. The frequency of accidents resulting in the discharge of the contents into water has been low. However, there is still the finite probability that these accidents will continue to take place. Once such a spill has occurred there is an immediate need to predict the concentration profile of the chemical as it travels down the river. The resulting concentration must than be matched with the known toxicological and other properties of the material so that appropriate action may be taken to alleviate any potential hazard.

The types of questions facing the individual who must make the necessary decisions are:

1. What are the properties of the spilled material? e.g. How flammable is the chemical? What are the key acute toxic characteristics?
2. What concentrations can be expected downstream?
3. How long will the concentrations persist at any one point?
4. What is the significance of these concentrations? Should downstream users of the water be concerned and if so for how long?

A computer program, called rSPILL, that works on most personal computers has been developed to answer the above questions. The remainder of this article will describe in general terms how this program operates. For more information please contact the author at the above address.

WHAT HAPPENS DURING A SPILL?

As a chemical is released into a river there are several forces that begin to operate, all of which must be considered. For materials that are partially soluble and are heavier than water there is the additional problem of determining the rate and extent of solubilization. The computer program is capable of estimating both the fraction of chemical that goes into solution as well as the dispersion forces acting on the chemical. As the peak moves these forces continually dilute the chemical until finally a point is reached where the concentration becomes uniform across the width of the river.

In addition to the above dilution processes the material may be lost from the water column via evaporation. The program contains state of the art techniques in modeling evaporation. Finally, consideration must be given to the reactions that eventually degrade the added material back to carbon dioxide, water and inorganic constituents (commonly referred to as "mineralization"). While most of these types of degradation reactions are too slow to have much influence on the resulting concentration they will be important in predicting the ultimate fate of the added chemical. Where known the rate of hydrolysis, photodegradation and biodegradation are included in the data package.

All of the above reactions have been formulated into rSPILL. Thus by entering easily available data on the river, the name of the chemical and how much was spilled a profile is quickly generated illustrating how the concentration varies with distance downstream as well as the gradient across the width of the river (1-3).

THE DATA BASE AND RISK ASSESSMENT

In order to finish the task of evaluating the impact that the spill will have on the water quality a data base of key properties must be readily available. In many ways the unique feature of rSPILL is not the ability to generate a concentration profile but the ability to quickly locate and interpret chemical and biological data. The data that has been assembled includes key properties such as:

Physical Data
  Molecular Weight
  Melting Point
  Boiling Point
  Specific Gravity
  Solubility in Water
  Vapor Pressure
  Flash Point
  Degradation Rates

Biological Data
  Microbiological Degradation
  96 hr. LC50 for fish
  Acute and Chronic LD50 for rats
  Threshold Limit Value (4)
  Carcinogenic Risk (5)
  Odor Value from water (6)

In addition to the above there are several interpretative statements that are made for each chemical. It is through these interpretations that the task of evaluating the potential hazard resulting from a spill is made easier. A typical example of the data is illustrated in the printout for Ethylene Dichloride in Figure 1.

It should be noted that the three numbers listed in Figure 1 (the upper right hand corner) are:

1. The Hazard ID No. which is a four digit number assigned by the Department of Transportation (7) to many of the hazardous chemicals that are shipped by bulk. The number has been accepted by all transportation carriers in North America and the United Nations. Accordingly the number may be prefixed with the initials NA or UN. During an actual incident it may be the one means of identifying the contents of the spilled material.

2. The CAS Number is assigned by Chemical Abstracts and allows the user to access that data base.

3. In a similar manner the TOX No. allows the analyst to locate the toxicological information published in the Registry of Toxic Effects by NIOSH (5).

The assumptions involved in using the data will be discussed under the following headings.

I. Solubility
II. Flammability
III. Volatility
IV. Estimating Safe Concentrations for Humans Drinking Water.
V. Estimating Vapor Pressure
VI. Estimating Odor Threshold for the Water Temperature of Interest
VII. Estimating Evaporation Rate Constant as a Function of Wind Speed
VIII. Estimating the Amount of a Chemical going into Solution
IX. SMILES-A code for Chemical Structures

Sections I-IV are used to make the interpretative statements appearing on the Data sheets for each chemical (Figure 1 is an example). Sections V-VIII are used in developing parameters that more closely reflect the environmental conditions surrounding the site of the accident. The last Section describes a code for characterizing chemical structures.

```
                  -----------------------
                 | ENVIRONMENTAL   DATA |
                 |        No. 16        |
                 |     03-16-1987       |
                  -----------------------

ETHANE *1,2-DICHLORO                  HAZARD ID.No.:1184
                                      Cas No.      :107-06-2
                                      Tox No.      :KI 05250


Synonym :ETHYLENE DICHLORIDE
Other Properties:
Code  :ClCCCl

                   PHYSICAL PROPERTIES

MOLECULAR WEIGHT                      =99
MELTING POINT                         =-35 (8) C
BOILING POINT                         =83.5 (1) C
WATER SOLUBILITY (20'25'C)            =8690 (8) MG/L
SPECIFIC GRAVITY                      =1.25 (8)
FLASH POINT                           =18 C
VAPOR PRESSURE (20'-25'C)             =.08 (8) ATMOSPHERES
LOG KOW                               =1.79

                 TOXICOLOGICAL PROPERTIES
MATERIAL IS CONSIDERED TO BE PERSISTENT BY THE BOD TEST
96-HR FISH LC50                        =500 MG/L
RAT LD50                               =670 (3) MG/KG
ODOR THRESHOLD FROM WATER AT 60'C      =2.8 (5) MG/L
OSHA VALUE FOR THE TLV                 =50 (4)  PPM
MATERIAL IS AN ANIMAL CARCINOGEN (3)

                INTERPRETATIVE STATEMENTS
LIQUID IS EXTREMELY FLAMMABLE
LIQUID IS SLIGHTLY SOLUBLE
ESTIMATED 2-WEEK SAFE LEVEL FOR HUMANS IS 30.31 MG/L IN
                    THE DRINKING WATER
LIQUID HAS HIGH VOLATILITY
** CHEMICAL IS CLASSIFIED D (9) BY USEPA UNDER SPILL REGS **

Revised: Jan 1987
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Figure 1 Illustrating the type of Data stored in rSPILL. (The numbers in parenthesis refer to an internal listing of references that are an integral part of the program.)

I. Solubility

Solubility of a chemical ranges from being soluble in all proportions to being essentially insoluble in water. For purposes of classification, a material soluble only to the extent of 0.1% will be referred to as insoluble. This is a convenient cut-off since it matches the toxicological criteria for the retention of materials in the lung. Given this lower limit the scheme shown in Table 1 has been developed to categorize solubility.

TABLE 1
Classification to be used in Characterizing the Solubility of Chemicals

Category	Solubility(mg/l)
1.Insoluble	<1000 (<0.1%)
2.Slightly soluble	1000-50,000
3.Moderately soluble	50,000-100,000
4.Very soluble	100,000-1,000,000
5.Miscible	>1,000,000

II. Flammability

The extent to which a material is flammable is based on the flash point(FP).

Extremely flammable--are those chemicals where the FP is < 23 C . Diethyl ether would be an example of such a chemical.

Flammable--chemicals that have a FP < 38 C (Acetone).

Combustible-- materials such as kerosene where the FP is < 93 C.

Non-Flammable-- are those chemicals whose FP is above 93'C such as propylene glycol

III.Volatility

Once a chemical is spilled into a water system there is a possibility for the material to be lost to the air via evaporation. A technique has been developed to calculate the rate at which the organic will leave the water compartment(8). This is based on a knowledge of the vapor pressure and the water solubility. Where such data is available the following calculations have been made.

a. Henry's constant, which is the ratio of the concentration in air to the concentration in water.

b. The rate constant for evaporation.

The amount of chemical in the air surrounding the spill site will be a combination of Henry's constant and the rate at which the organic leaves the water. For example, a fast rate combined with a large Henry's constant will give a high atmospheric concentration. It is possible by plotting these two values to arbitrarily identify three groups.

A. The volatile group is characterized by Henry's constant greater than .007 with a rate constant >.01 m/hr. The materials so identified will have a potential for yielding reasonable atmospheric concentrations.

B. The next group will be classified as intermediate in volatility. This implies that it will take a higher water concentration to yield a noticeable atmospheric concentration.(i.e. $k>1 \times 10^{-5}$ and $H > 5 \times 10^{-6}$

C. The remaining materials are non volatile and will be confined to the water into which they were spilled. Incidentally an avenue other than evaporation will have to be found for cleansing the water of such chemicals.

The plot of k vs H is shown in Figure 2 for the chemicals in Table 2.

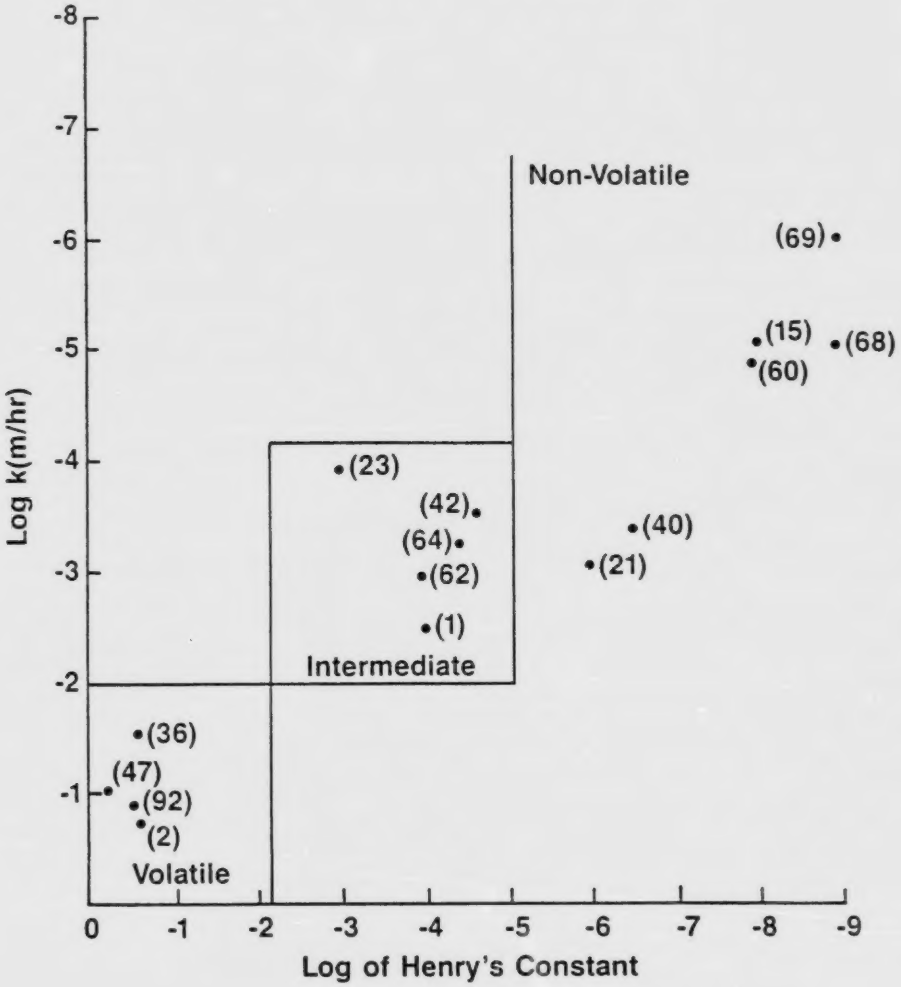

Figure 2. A plot of k vs Henry's Constant for the chemicals in Table 2.

TABLE 2

A List of Chemicals with their Henry's and evaporation rate constant in m/hr at 20 C.

Name	Number	Henry's Constant[a]	k (m/hr)[b]
Volatile			
Vinyl Chloride	51	130	.16
Trichloroethylene	49	.37	.11
Toluene	92	.32	.13
Tetrachloroethylene	47	.83	.10
Styrene	45	.086	.12
Methyl Chloride	36	1.4	.18
Ethylene Dichloride	29	.04	.11
Ethyl Benzene	26	.41	.13
Methylene Chloride	39	.13	.13
Epichlorohydrin	25	1.11	.14
Diphenyl Oxide	20	.01	.04
p-Dichlorobenzene	13	.08	.09
Diphenyl	19	.01	.05
o-Dichlorobenzene	12	.06	.09
Chloroform	11	.12	.11
Chlorine	10	.02	.10
Carbon Tetrachloride	9	.99	.11
Benzene	3	.23	.14
Allyl Chloride	2	.46	.15
Intermediate			
Acetone	1	2×10^{-4}	3.6×10^{-3}
iso-Butanol	6	5×10^{-4}	9×10^{-3}
n- Butanol	7	3×10^{-4}	5×10^{3}
Dowanol PM	23	1×10^{-3}	1.4×10^{-4}
Ethylene Diamine	40	9.8×10^{-4}	1.4×10^{-4}
Phenol	42	2.2×10^{-5}	3×10^{-4}
MCP amine	64	8.8×10^{-5}	7×10^{-4}
Chlorpyrifos	62	1.7×10^{-4}	1.2×10^{-3}
Non Volatile			
Tripropylene glycol	70	9.7×10^{-9}	8.9×10^{-6}
Triethylene glycol	69	9.7×10^{-10}	1×10^{-6}
Triethanol amine	68	9.7×10^{-10}	1×10^{-5}
Ethyl acrylate	63	1.3×10^{-7}	1.6×10^{-4}
Dipropylene glycol	60	9.7×10^{-9}	1.1×10^{-5}
Chloroacetyl chloride	58	1.3×10^{-6}	1.6×10^{-3}
Propylene glycol	44	1.2×10^{-7}	1.8×10^{-4}
Monoethanol amine	40	3.9×10^{-7}	6.4×10^{-4}
Dowanol EE	22	5.2×10^{-6}	7×10^{-7}
Ethylene glycol	30	1.2×10^{-7}	1.9×10^{-4}
Dowanol EB	21	8.6×10^{-7}	1×10^{-3}
Diethanol amine	15	9.8×10^{-9}	1.2×10^{-5}

[a] H is Henry's constant which represents the ration of the air concentration to the water concentration

[b] k is the rate constant for the evaporation from water to air.

IV.Estimating a two week safe level for humans (9)

Estimating a safe concentration in water for humans is based on converting the Threshold Limit Value (TLV) in air to an acceptable daily intake from water. In order to equate the body burdens from these two routes of exposure the following assumptions must be accepted.

1. The penetration of a chemical from air through the lung into the blood stream is a function of the solubility. For the purpose of the calculation the list of retention factors shown in Table 3 will be used. The more soluble the material the greater chance that the chemical will enter the blood stream and hence add to the body burden. A typical calculation is shown in Figure 3.

TABLE 3

Lung Retention Factors Based on Solubility

Solubility(mg/L)	Retention Factor
<1000	0.01
1000-50,000	0.3
50,000-100,000	0.5
>100,00	0.8

2. For a 70 kg man engaged in normal work activity about 10 m^3/day of air is inhaled for a 8 hour work day
3. It will be assumed that a normal person drinks 2 liters of water a day.
4. A 10-fold safety factor in favor of man will be applied to the final estimation.
5. In drinking water it will be assumed that 100% of the chemical will be absorbed into the blood stream.
6. In the case of a spill into a flowing body of water it is assumed that the contamination at any given point will persist for only a few days. Thus the values estimated should not be used as standards and they should not be applied to conditions where long term extended contamination is to be expected.

V. Estimating vapor pressure

The vapor pressure estimations were made from the procedures described by Lyman et al (10) and discussed by Grain (11) will be used. This assumes a correlation between the heat of vaporization and temperature. The resulting equation gives a satisfactory vapor pressure prediction for most solids and liquids.

extent of solubilization. This problem has been studied by Thibodeaux(14) and was discussed by Neely et al (15). As these solids or liquids are added to water, dissolution commences immediately on contact and continues to occur on the globules during transit to the bottom. Once on the bottom the material can form pools. Some of these pools may be protected from the turbulent action of the river and will form a reservoir which will slowly be solubilized into the water over a long period of time.

In the case of a spill only the portion that goes into solution immediately is of concern. Thibodeaux (14) has made an excellent start at predicting the rate from physical properties. Until these models are perfected only a crude estimate may be made at this time. This will be based on the study of the chloroform accident (15). From an analysis of the mass involved it was estimated that about 15-20 % of the original chemical went into solution. The remainder was in pools on the bottom and contributed to the long residual tail that was observed downstream from the spill (15). By assuming that miscible materials go into solution quickly as compared with 20% for chemicals similar to chloroform Table 4 can be easily formulated. The solubility classifications are identical to what have been used in other sections of this manual. Recognizing that the fractions assigned are arbitrary it appears to be a reasonable first approximation of what will occur during a spill. Obviously this is an area that needs further study. As more information becomes available it will be incorporated into this rSPILL.

Table 4
Estimating the amount of material solubilized based on solubility

Class	Solubility	Fraction
Insol	<1000	0.05
Sl.Sol.	1000-50000	0.20
Mod.Sol.	50000-500000	0.5
V. Sol.	500000-1,000,000	0.8
Miscible	>1,000,000	1.0

Chemicals that are lighter than water and insoluble will float on the surface. For soluble materials specific gravity will not be too important. At present the assumption is made that the amount of chemical going into solution from the floaters will be the same as for those chemicals that sink to the bottom (see Table 4). A warning statement is issued on the predictions that are made for potential "floaters". This message reminds the user that specific gravity may have an impact on the final results.

IX. Smiles

SMILES (Simplified Molecular Input Line Entering System) is a language for coding chemical structures. The system was developed by the Pomona College Med. Chem. Project in Claremont California. SMILES is easily learned and is subject to only a minimum set of rules. For more information refer to Reference 16.

CONCLUSION

rSPILL provides a convenient, fast method for analysing the events surrounding a discharge of a chemical into a river. Through such an analysis the individual with safety responsibility will have some information on which to base the hard decisions that must be made.

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LABORATORY EXPERIMENTS ON AN EXTERNALLY-HEATED PRESSURE LIQUEFIED GAS CONTAINER

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ABSTRACT

Experimental results from an externally-heated cylindrical horizontal pressure liquefied gas container with a pressure relief valve is described. Thermohydraulic behavior is analyzed from the pressure, temperature, and mass discharge measurements.

INTRODUCTION

Pressure liquefied fuels are widely used in domestic, commercial, and industrial installations. An increase in the consumption of such fuels within Canada has been encouraged by the Federal Government [1]. Their usage requires transportation and storage of considerable quantities. Transportation is primarily by rail and road tank cars. A number of recent accidents involving storage tanks/transport vehicles has produced extensive property damage, serious personal injury and many deaths. Major evacuations have also been necessary in some cases. One incident in Mississauga caused the evacuation of almost a quarter of a million people for a period of five days [1]. On November 19, 1984, a sequence of events at the LPG-facilities in San Juan Ixhuatepec, Mexico City, led to one of the greatest disasters caused by an industrial activity. This accident caused over 500 deaths and resulted in 7000 being severely injured [2].

In a typical railway accident, a tank car carrying a pressure liquefied gas (e.g., propane, LPG) is punctured due to a derailment impact. The flammable commodity is subsequently ignited by sparks or a hot component. The resulting fire may project onto or engulf other tanks. Unless vented by suitably-sized relief valves, the tanks would pressurize while heating up and would ultimately fail and likely explode. Even if the tanks were to vent their contents through the pressure relief valve (PRV), the vapour space heat transfer is so poor that the tanks may still fail. The explosions are often severe with major pieces of the containment vessel being propelled up to 1 km from their initial locations [2]. This type of phenomenon is termed Boiling Liquid Expanding Vapour Explosion (BLEVE). The flying debris may cause secondary fires between their origin and destination. Large vapour cloud explosions and fire balls can also result [3].

TEST APPARATUS

The experimental facility employed consisted of a horizontal, double-walled, pressure vessel with a capacity of 37.4×10^{-3} m^3 (Figure 1). The cylindrical portion of the inner tank can be electrically heated. The test tank is fitted with a PRV and a 25 mm thick transparent window for visual observation. The PRV

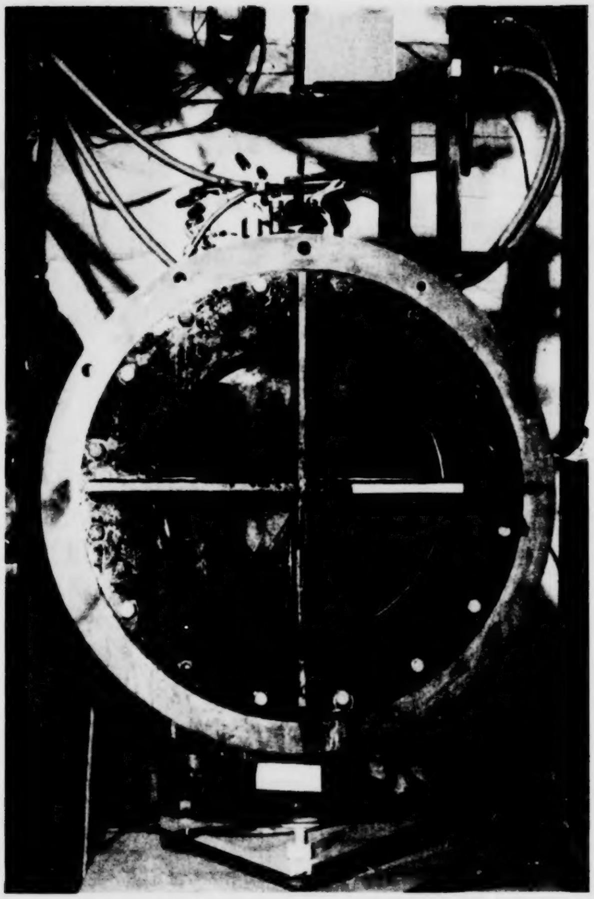

Figure 1. Photograph of test apparatus

is operated by an air cylinder, the air supply being computer-controlled by four solenoid valves. The PRV may be oriented at any angle to simulate a variety of valve locations under a transportation tanker accident condition.

Measurement instrumentation includes up to 50 thermocouples of iron or copper/constantan (J or T types) and a pressure transducer in the vessel and in the PRV ducting. The mass of the tank and its contents is measured by means of a load cell. Valve efflux thrust is also measured using a sensitive load cell. An HP 9220 minicomputer acts as the overall system controller (Figure 2).

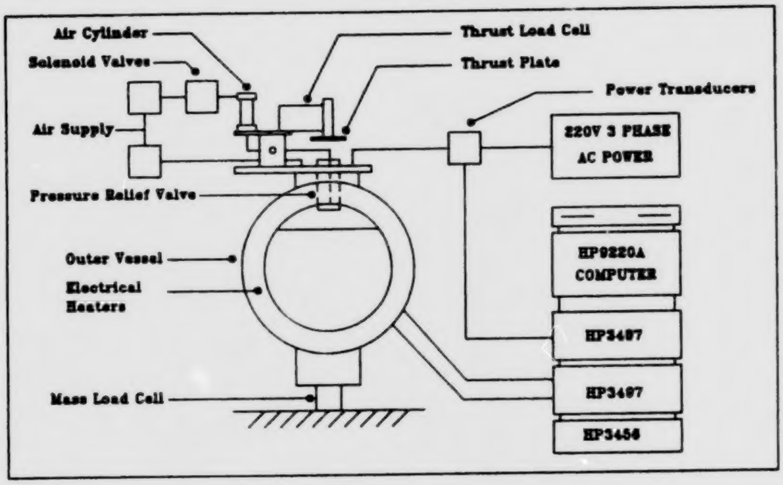
Air Cylinder
Solenoid Valves
Air Supply
Pressure Relief Valve
Outer Vessel
Electrical Heaters
Mass Load Cell
Thrust Load Cell
Thrust Plate
Power Transducers
220V 3 PHASE AC POWER
HP9220A COMPUTER
HP3497
HP3497
HP3456

Figure 2. Schematic diagram of the experimental set-up

Heater power (0-80 kW_e/m^2) is maintained by use of three manually-controlled 220V 3-phase variacs plus two 110 V, single-phase variacs. In order to prevent a possible failure of the heated and pressurized inner tank the annulus is maintained at a pressure in excess of the inner tank. The heater elements may be controlled together or individually to simulate pool or torch fire heat flux distributions. Additional information on the experimental apparatus may be obtained from several original theses [4,5].

TEST PROGRAM

The lading used from the experiments reported here was Refrigerant 11 (tri chloro fluro methane). The PRV was set to open at 241 kPa g and close at 229 kPa g.

A test program was implemented using a variety of liquid fills (25-90%), power levels (40, 60 and 80 kW_e/m^2), PRV orifice diameters (6.35-9.54 mm) valve orientations (0^o, 60^o, and 120^o from vertically upright).

In addition, further tests are being made with mixtures of R11, R12, and R13 to simulate the behavior of mixtures such as LPG.

Thermohydraulic Behavior

From commencement of uniform heating with the valve vertical (0^o), the heat transfer to the liquid and vapour is initially by free convection. In the vapour space, this convection leads to significant vertical temperature gradients caused by the stratification and reduction, with time, of fluid motion.

The liquid space convection is complex [6,7]. Wall heating causes a region of instability located in a bottom sector and the development of wall boundary layers thereafter. These layers impact with the free liquid surface, turn horizontally, and form a stratified layer whose surface temperature increases with time and is responsible for system pressure. The large subcooled core of liquid receives energy from the bottom of the tank and the exterior edges of the boundary layers. The heat transfer from the vapour space walls also influences the interface temperature by radiant exchange; additional effects are also caused by non-condensible gases or impurity components such as ethane or butane in LPG. The liquid stratification is influenced by initial lading fill and heating and the interaction with geometry, instability angle, and boundary layer interaction.

Dependent upon the incident wall heat flux and fluid composition with liquid space wall heat transfer moves rapidly from laminar to turbulent free convection, thence to saturated and next subcooled nucleate boiling. The pressure is set by the liquid surface temperature and composition with condensation and evaporation taking place so to adjust to equilibrium conditions at the interface. With time, as heating continues, pressure increases and reaches the PRV opening point. Material is now discharged and pressure affected. The resulting pressure response is dependent upon valve orifice size and position. With a vertical valve, the initial discharge is superheated vapour; however, fill and subsequent liquid interface behavior governs further discharge quality. Large fills, orifice sizes and stratification cause significant flashing and swelling of the affected regions. The stratified region is now partially superheated relative to the instantaneous system pressure and the wall boundary layer. Swelling of the stratified and possibly subcooled core regions can cause liquid carry over and entrainment resulting in a significant two-phase discharge through the valve. This discharge may result in significant rates of pressure increase if the device is improperly sized and a two-phase choked flow may result. As venting continues the temperature of the subcooled core and stratified regions become homogeneous. Ensuing thermohydraulic response is now dependent upon whether pressure is increasing or decreasing; with increasing pressure the contents become subcooled and wall subcooled boiling is the major source of vapour generation; with decreasing pressure, homogeneous nucleation results in saturated boiling throughout the liquid.

As material continues to exit from the valve, the level of two-phase material in the tank decreases until finally vapour-only flow results. With continued heating, the tank eventually empties and the valve reseals. With decreasing fluid levels, exposed walls rapidly increase in temperature due to the poor vapour space heat transfer. Tank wall failure at this time may result in a BLEVE if significant amounts of lading remain.

RESULTS

Figure 3 gives a typical pressure-time response curve for a test with 80% fill, 80kW/m^2 of electrical heat, and the PRV vertically up. The pressure rises steadily as the tank contents heat, until the PRV opening set point of 241 kPa g (35 psi g) is reached. The valve then opens, and closes at a set point of 229 kPa g (33.25 psi g) under operation of the two-position controlled valve. This valve is operated by the data acquisition system with a frequency of 1 Hz. The valve cycles a few times and then remains open continuously.

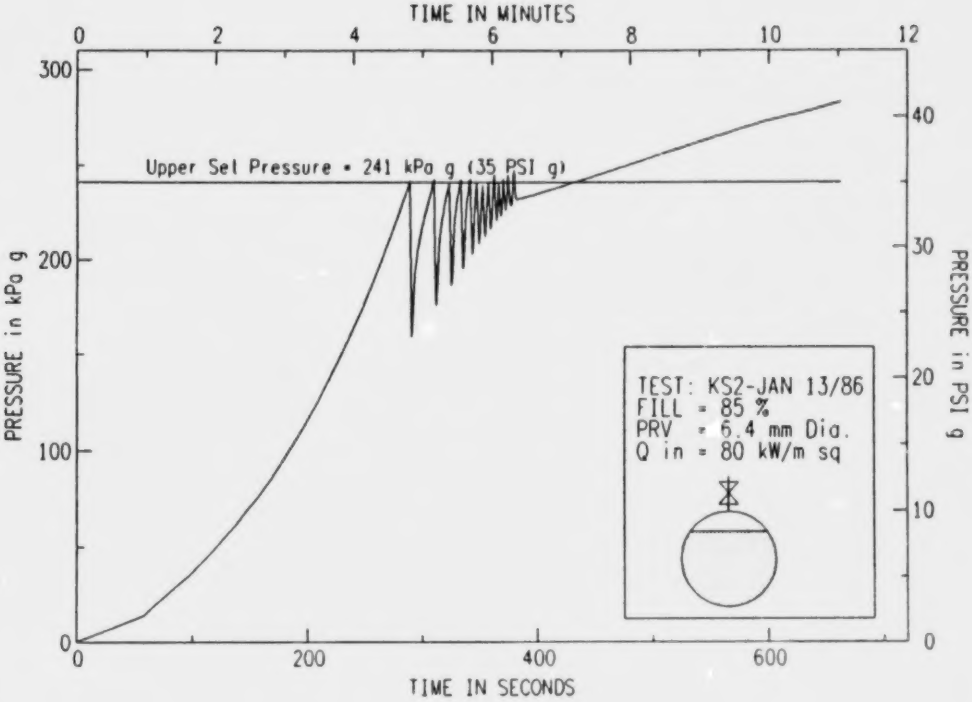

Figure 3. Typical pressure history

Figure 4 gives the mass of tank and contents as a function of time for three valve orientations, with a volume fill of 85%. As may be expected, the rate of mass efflux is a function of quality of discharge. The higher the exhaust quality, the lower the discharge rate. Analysis of the two-phase discharge is complex since the flashing flow is choked.

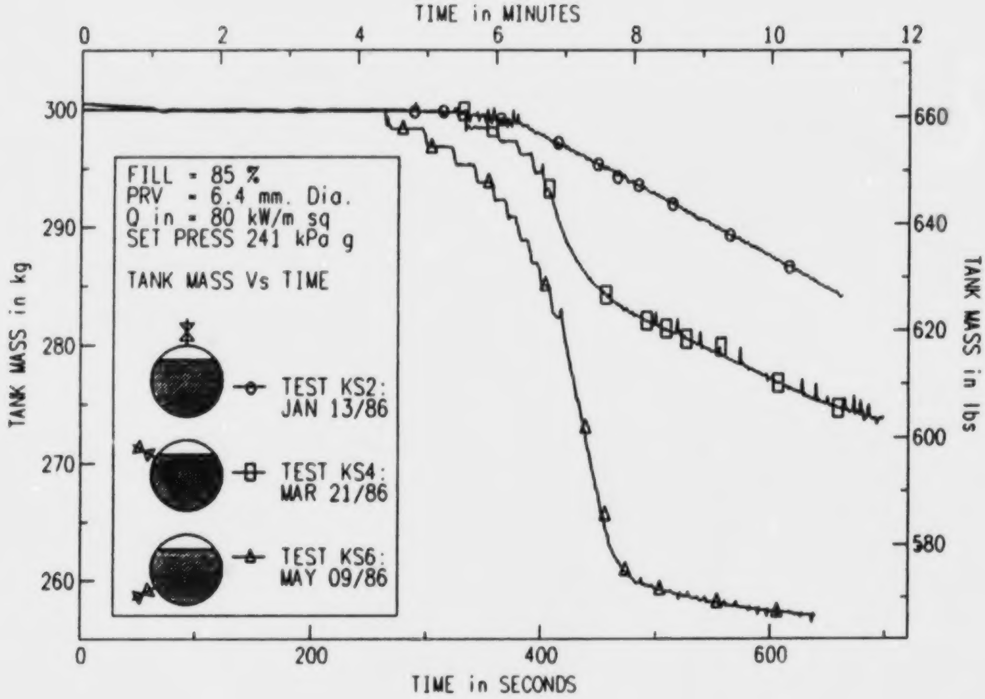

Figure 4. Mass of container versus time of heating for PRV at three circumferential positions

Figures 5 and 6 present the temperatures of liquid and vapour walls, respectively, for three test with valve orientations as shown. Vapour space wall temperatures become extremely high, where liquid wall temperatures remain slightly above the saturation for the prevailing pressure inside the tank.

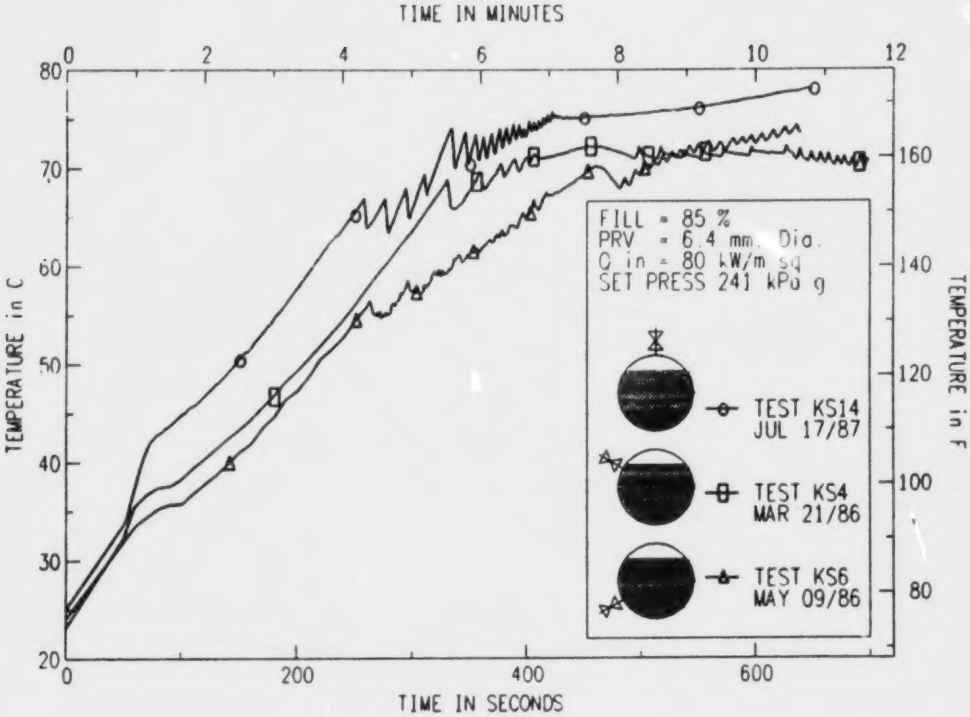

Figure 5. Temperature of liquid walls versus time of heating

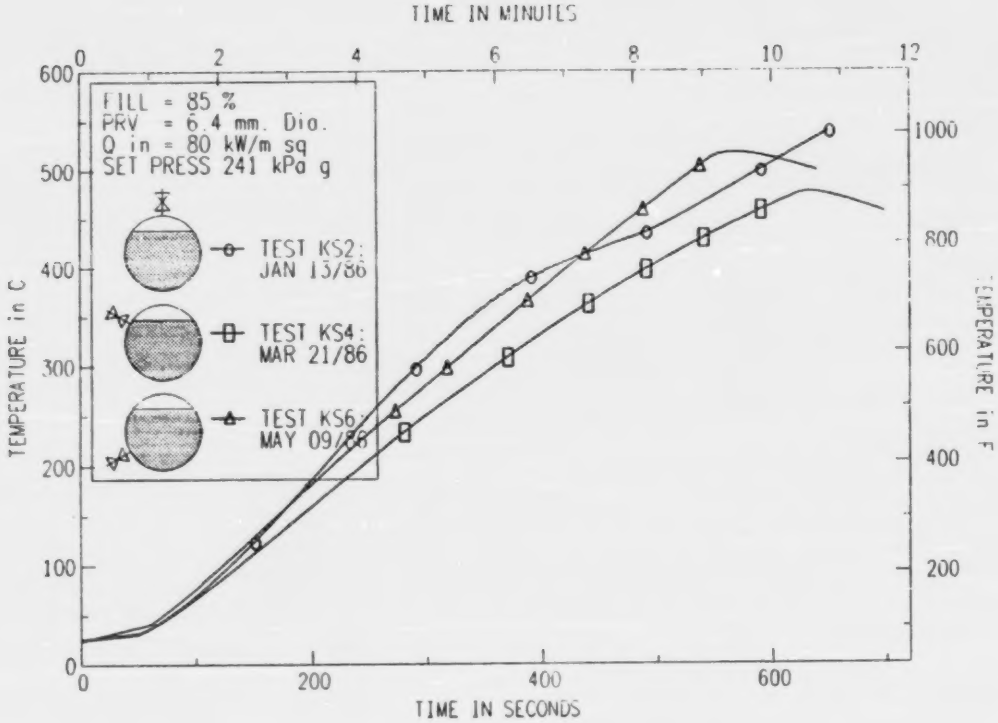

Figure 6. Temperature of vapour walls versus time of heating

Figures 7 (a) and (b) illustrate the development of stratification both in the liquid and vapour for two tests. For the test shown in Figure 7 (a), the first valve opening occurs at 250 s, it then takes over 100 s for the core of the tank to reach saturation temperature. Visual observation of subcooled boiling during the first few valve openings confirms this data.

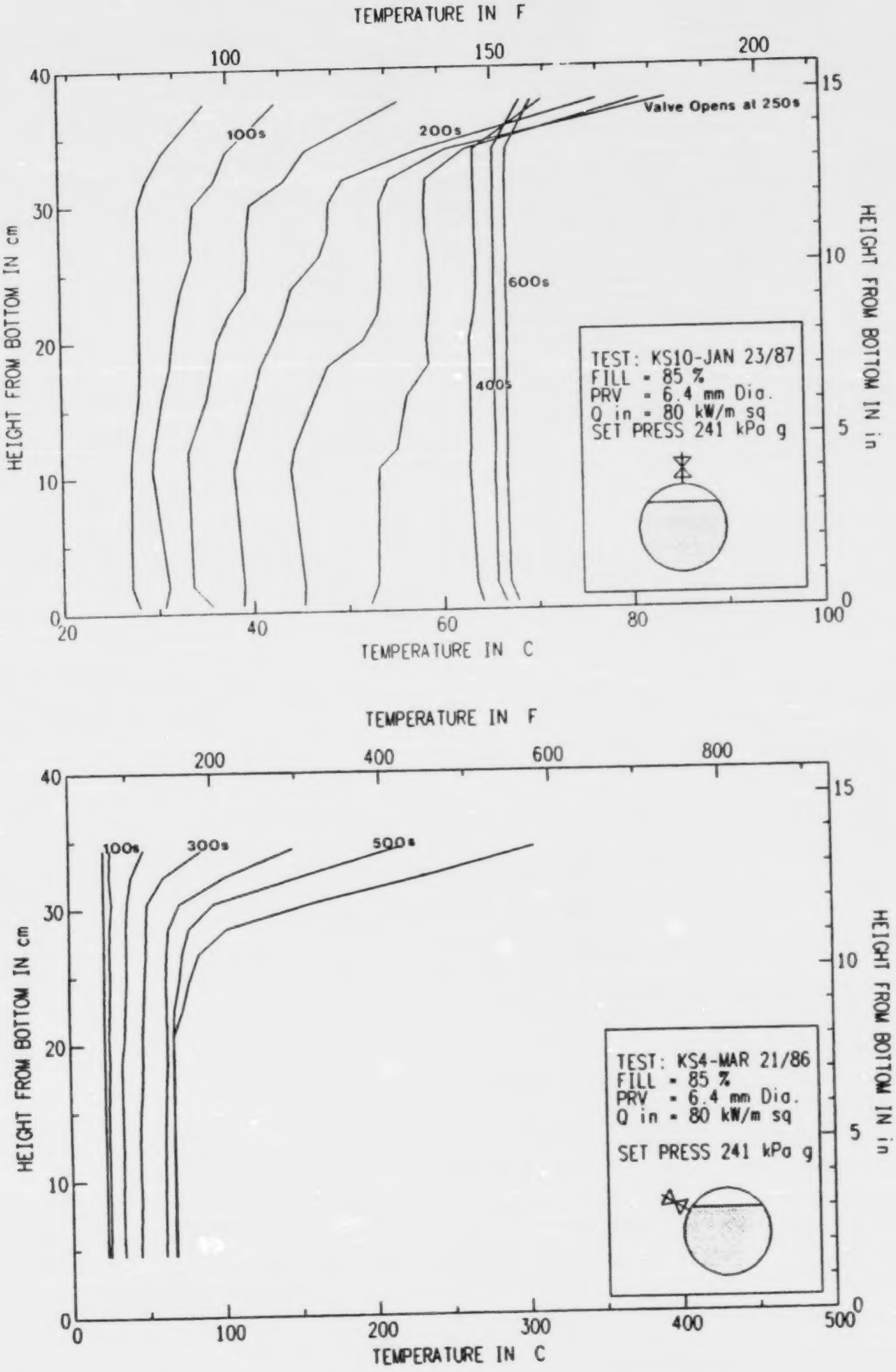

Figure 7. Liquid and vapour temperature as function of height versus temperature (a) PRV - up-right; (b) PRV - tilted by 60°

In Figure 7b, where the PRV was tilted 60° from the vertical, shows that stratification in the vapour space was severe, and indicates that the region above the valve position was virtually stagnant. This phenomenon, too, is confirmed by visual observation.

Measurements of void fraction development were carried out both in the bulk and wall regions of the vessel with and without pressure relief. An example of this data is given in Figure 8 and 9. In Figure 9, the pressure, mass and swell height of a test is shown. After initial valve cycling, the PRV remained open to the termination of the test. Figure 9 illustrates the radio frequency boundary layer void fraction measurements. The two probes, P9 and P12, make measurements in liquid and vapour wall regions. The effect of the two-phase swell or frothing is shown in the behavior of probe P9, which becomes successively covered and uncovered with vent cycling. With the onset of venting, the probe shows the effect of two-phase coverage which is followed by subsequent uncovering of the probe due to valve efflux.

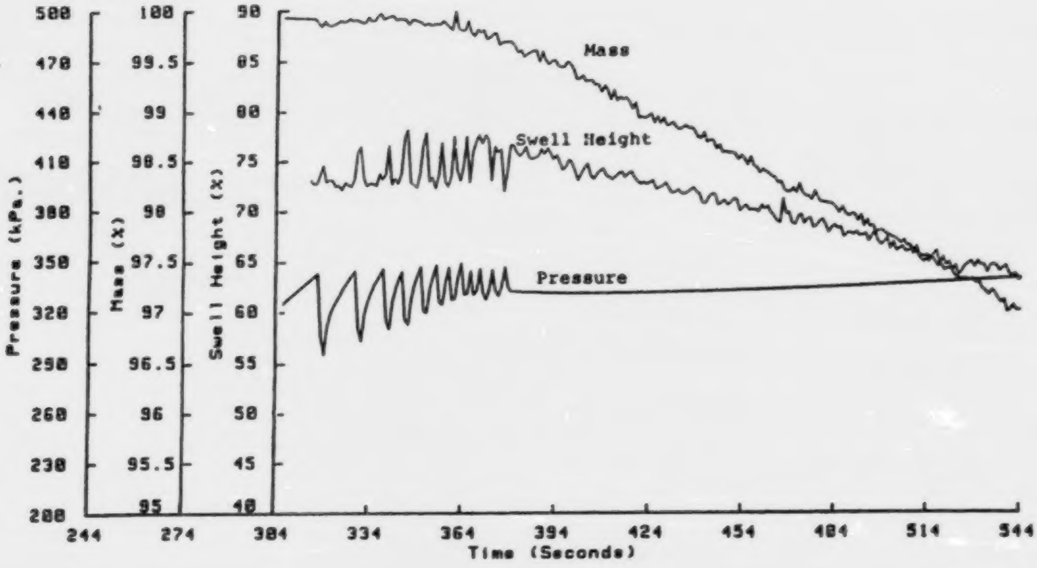

Figure 8. Pressure, mass and swell height variation, WQ2

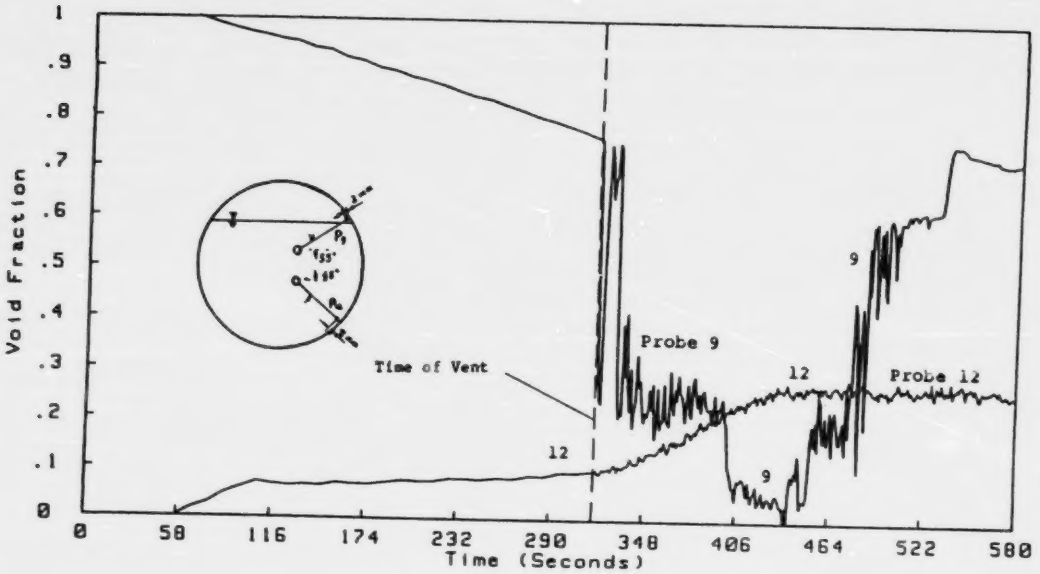

Figure 9. Wall void fraction development, WQ2

Video Records

Time-synchronized video records are made of each test and a complete film sequence made from selected tests is available on loan from the authors. The data are used to complement the analysis of basic phenomena, stratification, mass efflux, swell height, and void development.

CONCLUSIONS AND FURTHER WORK

A comprehensive series of experiments has been performed and described which present an understanding of the thermohydraulic response of pressure liquefied gases in partially-filled horizontal cylinders exposed to external heating and protected by PRVs. These test results have now to be analyzed in detail for stratification, phase separation and distribution [5,10], and two-phase critical flow [8,9]. Further experiments to determine the effects of impurity and non-condensible gases, non-uniform heating and circumferential sloshing are to be conducted.

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THE USE OF SPREADSHEET AND GRAPHICS SOFTWARE FOR INTERPRETING THE RESULTS OF A CHEMICAL SPILL IN PONDS AND LAKES

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ABSTRACT

A chemical fate model based on the concept of fugacity, QWASI (Mackay et al, 1983), is applied to results of a simulated chemical spill using LOTUS 1-2-3 on a microcomputer. This software package is shown to provide a powerful, easy to use framework in which to use QWASI. In an example using data from a simulated spill of tertiary butylphenyl diphenyl phosphate (t-BPDP), the graphics capabilities and interactive features of LOTUS 1-2-3 are used to guide the modeller regarding the influence of various processes on the fate of the chemical, and to determine appropriate variables on which to focus to improve the simulation.

INTRODUCTION

Numerous chemical spills occur every year and many of these result in discharges to aquatic environments. To quantify possible harmful effects and to undertake effective remedial measures, it is important to combine the results of experimental endeavours with a comprehensive environmental model.

When determining the fate of chemicals spilled in aquatic environments, measurements and observations should be made at several scales and levels of complexity, each of which presents its own advantages and disadvantages. Small scale, single-media, "beaker" laboratory tests allow variables to be well controlled but may not account for some important processes and interactions in the real world. However, full scale field experiments may not allow adequate control of variables and experimental conditions to permit defensible conclusions. Thus, investigations at all levels of control, scale and complexity are necessary including laboratory systems, lake enclosures and whole lakes.

Simulated spill experiments in mesocosms such as ponds, small lakes or enclosures in lakes offer a useful blend of real world conditions and control of variables. Numerous authors have reported results of tests of chemical spill fate in small scale ponds (Lau, 1985; Muir et al, 1985) and have interpreted the results to estimate chemical half-lives and determine the dominant processes. Because of well documented test conditions and results, such studies often lend themselves well to mathematical simulations of chemical spill fate but a recurring analytical limitation is that the chemical's "disappearance" may be due to volatilization, several degrading reactions, sedimentation or a combination of processes. Difficulty in discriminating between these processes inhibits the creation of a mathematical statement or mass balance which not only reflects observations, but accurately accounts for the relative importance of the processes. An accurate mass balance is essential if the model is to be applied to other systems for predictive purposes.

In this paper, a method of simulation is suggested which improves the ability of the modeller to examine systematically the influence of various processes in the environment being modelled, and to improve the simulation by focussing on appropriate processes. This is done by using a comprehensive model of chemical fate in aquatic systems, namely the QWASI (Quantitative Water Air Sediment Interaction) model (Mackay et al, 1983), programmed with microcomputer spreadsheet software to take advantage of its plotting capabilities and ease of use.

In principle there are two types of experiments which can be simulated. The mathematically easier and experimentally less frequent is a steady state system in which a chemical is continuously added to the system until a steady state is reached in which the sum of the loss rates equals the addition rate. More mathematically complex and more frequent (because it is experimentally easier) is an unsteady state system in which a batch of a chemical is spilled and its decay in water and sediment followed in time. In the steady state system the simulating mass balance equations are basically algebraic, whereas in the unsteady state case they are differential. The differential equations can be solved numerically or analytically. The QWASI model uses analytical equations to solve unsteady state conditions, avoiding some difficulties which can occur with numerical solutions.

The approach in this paper is to (i) describe the model briefly in terms of its underlying equations and processes simulated, and (ii) outline the sequence of steps in a typical simulation using the selected software.

MODEL DEVELOPMENT

Equations

This model has been fully described elsewhere (Mackay et al, 1983) and only a brief summary is presented here. Figure 1 illustrates the processes considered. To simplify the algebra, the use of fugacity is adopted instead of concentration as the driving force behind the processes (Mackay et al, 1983). The resulting equations can be treated in algebraically identical concentration terms. Definitions of the symbols used are given in Table 1.

For each medium, the concentration C (mol/m3) is related to fugacity f (Pa) using a fugacity capacity term Z (mol/m3) which is specific to the chemical, the medium and prevailing temperature. The relationship is that C equals Z*f. Values for Z are calculated from the partitioning and physical/chemical properties as shown in Table 2.

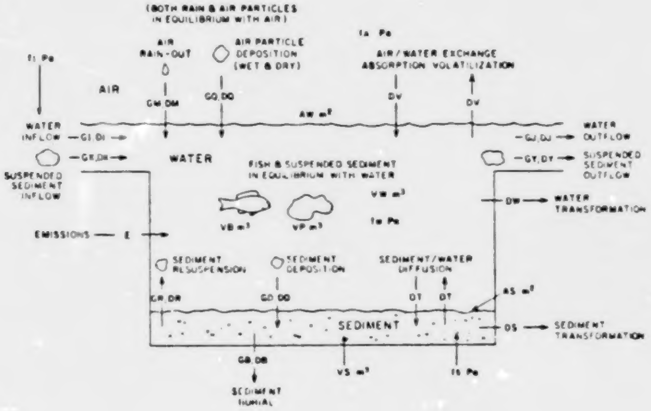
(BOTH RAIN & AIR PARTICLES IN EQUILIBRIUM WITH AIR)
fI Pa
AIR RAIN-OUT
AIR PARTICLE DEPOSITION (WET & DRY)
fA Pa
AIR / WATER EXCHANGE
ABSORPTION VOLATILIZATION
AIR
GM,DM
GQ,DQ
DV
DV
AW m²
WATER INFLOW
GI,DI
WATER OUTFLOW
GJ,DJ
GX,DX
WATER
GY,DY
SUSPENDED SEDIMENT INFLOW
SUSPENDED SEDIMENT OUTFLOW
FISH & SUSPENDED SEDIMENT IN EQUILIBRIUM WITH WATER
VW m³
DW
WATER TRANSFORMATION
VB m³
VP m³
fW Pa
EMISSIONS
E
SEDIMENT RESUSPENSION
SEDIMENT DEPOSITION
SEDIMENT/WATER DIFFUSION
GR,DR
GD,DD
DT
DT
AS m²
SEDIMENT
DS
SEDIMENT TRANSFORMATION
GB,DB
VS m³
fS Pa
SEDIMENT BURIAL

Figure 1. QWASI Fugacity Model Processes

Table 1
Definition of Symbols

	Quantity		Subscripts
A	Area (m^2)	A	air
C	Concentration (mol/m^3))	B	burial and biota
D	transport/transformation parameter (mol/Pa)	D	sediment deposition
E	emission (mol/h)	I	water inflow
f	fugacity (Pa)	J	water outflow
G	flow rate (m^3/h)	L	liquid phase
h	depth (m)	M	rain
H	Henry's Law Constant ($Pa.m^3/mol$)	N	sediment pore water
I	group of D variables	P	suspended sediment particles
J	flowrate per unit area ($m^3/m^2.h$)	Q	air particles
k	rate constant h^{-1}	R	resuspension
K	mass transfer coefficient (m/h)	S	sediment
L	length (m)	T	sediment water transfer
P	pressure (Pa)	V	volatilization
R	gas constant ($Pa.m^3/mol$ K)	W	water
T	temperature (K)	X	water particles inflow
U	velocity (m/h)	Y	water particles outflow
V	volume (m^3)		
W	width (m)		
Z	fugacity capacity ($mol/m^3.Pa$)		

Table 2
Definition of Fugacity Capacities

Compartment	Definition of Z ($mol/m^3.Pa$)	
Air	$1/RT$	$R = 8.314\ Pa.m^3/mol.K$ T = temperature (K)
Water	$1/H$ or C^S/P^S	C^S = aqueous solubility (mol/m^3) P^S = vapour pressure (Pa) H = Henry's law constant ($Pa.m^3/mol$)
Solid Sorbent (sediment, soil, or particles)	$K_{SW}\rho_S/H$	K_{SW} = partition coefficient (L/kg) ρ_S = density (kg/L)
Biota	$K_{BW}\rho_B/H$	K_{BW} = bioconcentration factor ρ_B = density (kg/L)

Table 3
QWASI Model Processes and Rate Expressions

Process		Rates	(mol/h)	D and	D Group
Sediment Burial	G_BC_S	$G_BZ_Sf_S$	D_Bf_S	$D_B=G_BZ_S$	D_1
Sediment Transformation	$V_SC_Sk_S$	$V_SZ_Sk_Sf_S$	D_Sf_S	$D_S=V_SZ_Sk_S$	
Sediment Resuspension	G_RC_S	$G_RZ_Sf_S$	D_Rf_S	$D_R=G_RZ_S$	D_2
Sediment-To-Water Diffusion	$K_TA_SC_N$	$K_TA_SZ_Wf_S$	D_Tf_S	$D_T=K_TA_SZ_W$	
Water-To-Sediment Diffusion	$K_TA_SC_W$	$K_TA_SZ_Wf_W$	D_Tf_W	$D_T=K_TA_SZ_W$	D_3
Sediment Deposition	G_DC_P	$G_DZ_Pf_W$	D_Df_W	$D_D=G_DZ_P$	
Water Transformation	$V_WC_Wk_W$	$V_WZ_Wk_Wf_W$	D_Wf_W	$D_W=V_WZ_Wk_W$	D_4
Water-To-Air Volatilization	$K_VA_WC_W$	$K_VA_WZ_Wf_W$	D_Vf_W	$D_V=K_VA_WZ_W$	
Water Outflow	G_JC_W	$G_JZ_Wf_W$	D_Jf_W	$D_J=G_JZ_W$	D_5
Suspended Sediment Outflow	G_YC_P	$G_YZ_Pf_W$	D_Yf_W	$D_Y=G_YZ_P$	
Air-To-Water Absorption	$K_VA_WP_A/H$	$K_VA_WZ_Wf_A$	D_Vf_A	$D_V=K_VA_WZ_W$	D_6
Air Particle Deposition	G_QC_Q	$G_QZ_Qf_A$	D_Qf_A	$D_Q=G_QZ_Q$	
Air Rain-Out	G_MC_M	$G_MZ_Wf_A$	D_Mf_A	$D_M=G_MZ_W$	
Water Inflow	G_IC_I	$G_IZ_Wf_I$	D_If_I	$D_I=G_IZ_W$	D_7
Suspended Sediment Inflow	G_XC_X	$G_XZ_Pf_I$	D_Xf_I	$D_X=G_XZ_P$	

It may be preferable to express certain material transfer rates on an area specific basis ($J\ m^3/m^2.h$), namely

$$G_B = J_BA_S,\quad G_R = J_RA_S,\quad G_D = J_DA_S,$$
$$G_Q = J_QA_W,\quad G_M = J_MA_W$$

Table 3 illustrates how process rates can be equivalently expressed as a function of concentrations or fugacity. In the latter case, "D" values are used such that the rate is D*f (mol/h) and D has the units of mol/Pa.h. D values can also be grouped as shown in Table 3 (D1 through D7) to represent aggregate rates of chemical transfer into or out of various compartments. An important feature of this is that processes which affect transport and transformation and which vary greatly in nature (eg. from biodegradation to volatilization) are expressed in a common system of units (D values) such that rates can be compared directly. It is assumed in the model that the amount of chemical present in the biota can be neglected in comparison with the amount in water, sediment and suspended sediment. Concentrations in water and sediment can be found from fugacities using CW equals fW*ZW and CS equals fS*ZS.

Concentrations of a chemical in the suspended sediment phase could also be found by assuming equilibrium between water and suspended sediment such that fP equals fW and CP equals fP*ZP.

Microcomputer Model

Microcomputer spreadsheet programs are well suited for interactive calibration and testing of models. LOTUS 1-2-3 was selected due to its combination of powerful features such as macro commands, its ease of use, and graphics capabilities but other spreadsheet software packages may also be used. The model is set up such that basic physical chemical data such as molecular weight, octanol/water partition coefficients, and variables related to reaction rates are entered. Using these inputs, calculations of D values and resulting concentrations in water and sediment are performed. Graphic illustrations are automatically generated using a macro command, displaying observed and simulated concentrations versus time for water and sediments. These graphs, and the structure of the spreadsheet, allow the modeller to assess rapidly the relative importance of different physical processes, for example advection or volatilization, and guide the user towards focussing attention on changes to appropriate inputs to improve the "fit" of the simulation. This iterative process requires the modeller to have estimates of realistic ranges of values to use for different inputs. If desired, the user may also complement the visual assessment of the simulation with a numerical approach. Mean and rms calculations are presented of (i) absolute, and (ii) percentage, differences between observed and predicted concentrations, using a set of concentrations at various time intervals.

MODEL APPLICATION

The QWASI worksheet was created with the assumption that the modeller would have a basic knowledge of the LOTUS 1-2-3 program. The spreadsheet is set out in two parts. One portion contains the variables, called basic inputs; the other portion contains the formulae and the results. There is space for a maximum of twenty data points each for the sediment and for the water.

Application of the model is demonstrated in this example.

(1) The basic physical chemical data (Lau, 1985; Muir et al, 1985) for the phosphate ester, tertiary butylphenyl diphenyl phosphate (t-BPDP) are entered into the spreadsheet. The model multiplies each of the basic inputs by an individual scaling factor to calculate a calibrated basic input. Scaling factors are initially set at a value of 1.

(2) The calibrated basic inputs are used to calculate secondary inputs. The model multiplies each of the secondary inputs by a scaling factor to calculate a calibrated secondary input. Scaling factors are initially set at a value of 1.

(3) The calibrated basic inputs and the calibrated secondary inputs are used to calculate the D values according to the formulae described in Table 3. The model multiplies each of the D values by a scaling factor to calculate a calibrated D value. Scaling factors are initially set at a value of 1.

(4) The calibrated D values are used to calculate the values for D groups according to the formulae described in Table 3. The model multiplies each of the D group values by a scaling factor to calculate a calibrated D group value. Scaling factors are initially set at a value of 1.

(5) Calibrated D group values are used to calculate concentrations in water and in sediment as described in the Model Development section.

(6) If the "Alt" key and the "w" key are pressed simultaneously, observed and predicted water concentrations versus time are plotted on the screen. Similarly, the results for sediment appear on the screen if the "Alt" key and the "s" key are pressed at the same time. For t-BPDP, the fit of the predicted values to the observations, shown in Figures 2 and 3, is clearly inadequate using the first guesses of physical chemical parameters.

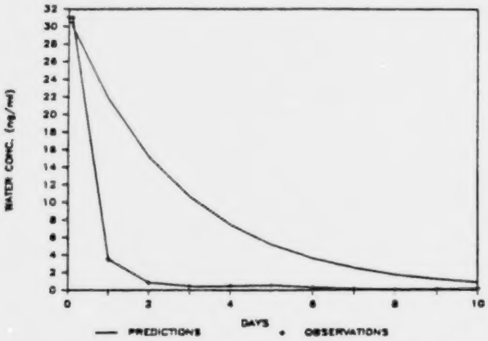

Figure 2. Concentration of t-BPDP in water samples.

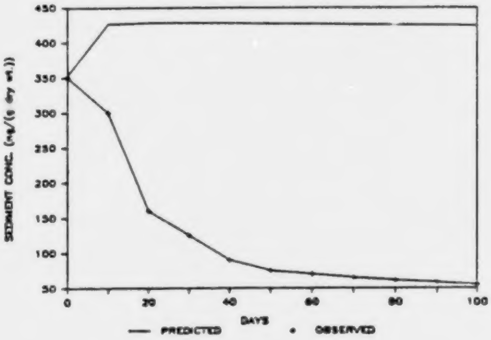

Figure 3. Concentration of t-BPDP in sediment samples.

Predicted values were calculated using initial estimates of physical chemical parameters with all scaling factors set to 1. Sediment and water transformation rate constants are 0/hour.

(7) After an examination of the graphs, the simulation may be improved by adjusting the D group scaling factors and reexamining the graphs. The decision of which scaling factors to change, and to what extent, requires the modeller to have an understanding of the processes affected by the D groups and reasonable limits to D group values.

If desired, a sensitivity analysis can be undertaken at this point by changing the scaling factors for the D groups, one at a time, by constant amounts (e.g. 0.1 or 10.0) to determine the sensitivity of the simulation to changes in each D group. This analysis allows a determination of which D groups (and thus which associated processes) are most important.

A sensitivity analysis performed for t-BPDP reveals that water concentrations were most sensitive to changes in D4, the D group for water transformation and water to air volatilization.

Sediment concentrations are not particularly sensitive to an order of magnitude change in any D group. Consequently, the modeller must supplement the results from the sensitivity analysis with additional information about t-BPDP in sediment. Disagreements between reported values of water and sediment transformation rate constants for t-BPDP (Lau, 1985; Muir et al, 1985) indicate that the modeller should focus attention on D1, the D group for sediment burial and sediment transformation.

(8) D group scale factors are adjusted until a satisfactory simulation is obtained. A scaling factor of 5 for D4 gives a good visual fit for water as shown in Figure 4. This indicates that D4 is actually 5 times larger than the initial estimate which produced the plot in Figure 2.

A scaling factor of 250 for D1 yields a good visual fit for sediment as shown in Figure 5. This indicates that D1 is actually 250 times larger than the initial estimate which produced the plot in Figure 3.

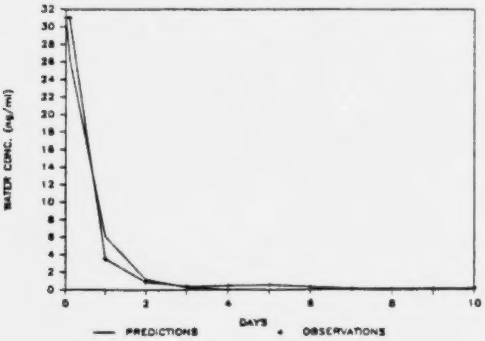

Figure 4. Concentration of t-BPDP in water samples.

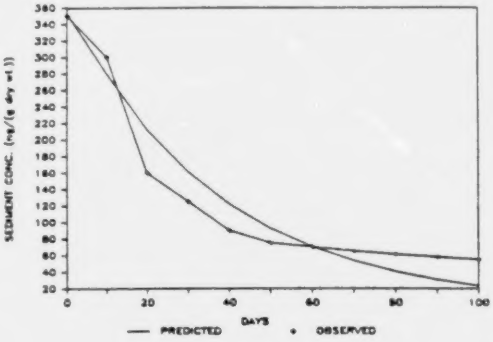

Figure 5. Concentration of t-BPDP in sediment samples.

Predicted values were calculated using initial estimates of physical chemical parameters with the scaling factor for D1 set to 250 and the scaling factor for D4 set to 5. Sediment and water transformation rate constants are 0/hour.

(9) The scaling factors for the D groups are reset to 1 and the modeller then examines which basic and secondary inputs (i) affect the D group values which had been assigned new scaling factors, i.e. D1 and D4 for t-BPDP, and (ii) have a large degree of uncertainty associated with their values.

The processes which are described by D1 and D4 are burial, sediment transformation, volatilization and water transformation. The disagreements mentioned in Step 7 between reported values of transformation rate constants indicate that the modeller should focus attention on these basic inputs.

(10) The scaling factors for the basic and secondary inputs that affect D1 and D4 are adjusted to improve the visual fit. It should be noted that to achieve a good fit by altering basic and secondary inputs, other D group values may also be affected.

In the first run of the simulation for t-BPDP, Figures 2 and 3, it is apparent that there are sinks in the water and in the sediment which are not properly represented. Values of zero, suggested by Lau (Lau, 1985), were entered initially for both the water and the sediment transformation rate constants. Changing the scaling factors on the transformation rate constants will not improve the simulation because any scaling factor multiplied by zero will yield a calibrated value of zero. Instead, new non-zero values for the transformation rate constants must be entered.

Muir, Lint and Grift (Muir et al, 1985) have measured pseudo first order half-lives of 0.44 days in water and 39 days in sediment. This corresponds to a water transformation rate constant of 0.0657/hour and a sediment transformation rate constant of 0.00074/hour. When these values are input, the simulation yields Figures 6 and 7, better visual fits than Figures 2 and 3 but not as good as Figures 4 and 5.

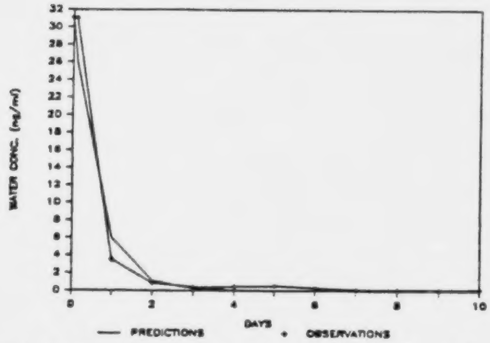

Figure 6. Concentration of t-BPDP in water samples.

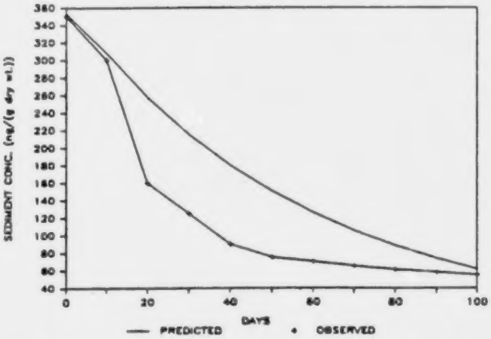

Figure 7. Concentration of t-BPDP in sediment samples.

Predicted values were calculated with all scaling factors set to 1. The water transformation rate constant is set at 0.0657/hour. The sediment transformation rate constant is set at 0.00074/hour.

(11) The graphs are visually examined and the simulation is enhanced by fine tuning basic inputs. The fit for water data, Figure 6, is good but the fit for sediment data, Figure 7, could be improved. Changing the scaling factor for the sediment transformation rate constant from 1 to 1.5 yields a good visual fit as shown in Figure 9. This means that the sediment transformation rate constant is 1.5 times larger under the experimental conditions used to obtain the observed data than under the conditions used by Muir et al. The corresponding graph for water is Figure 8.

The numerical estimates of mean and rms differences between observed and predicted concentrations can also be used by the modeller as indicators of the fit. For example, the observed t-BPDP concentration in water was on average 0.36 ng/ml or 58% higher than predicted. These numbers are useful but should be compared with caution to those from other simulations, since the modeller may be concerned with the model fit over a specific portion of the modelled time period, while the numerical calculations reflect the accuracy of the simulation over the entire time span. Thus a visual examination of the graphs is essential to assessing the adequacy of the simulation.

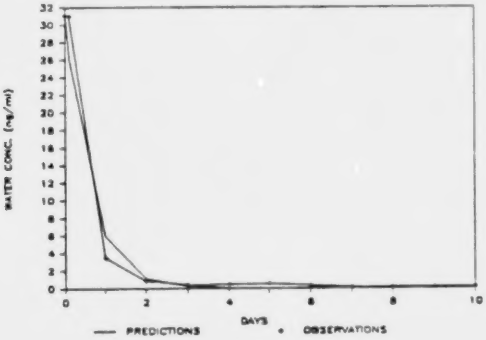

Figure 8. Concentration of t-BPDP in water samples.

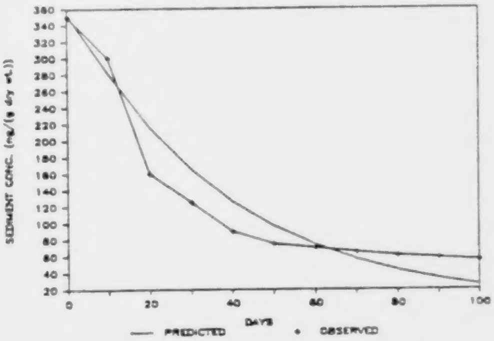

Figure 9. Concentration of t-BPDP in sediment samples.

The water transformation rate constant is set at 0.0657/hour. The sediment transformation rate constant is set at 0.00074/hour. The scaling factor for the sediment transformation rate constant is 1.5. All other scaling factors are set at 1.

DISCUSSION

The application of the model to t-BPDP demonstrates how this interactive spreadsheet helps the modeller to examine systematically the influence of various environmental processes. The sensitivity analysis of the D groups supplemented by the modeller's understanding of the processes affected by the D groups indicated that inputs associated with water and sediment transformation were the variables on which to focus. The visual fit for t-BPDP was improved by entering non-zero transformation rate constants. The simulation was enhanced by adjusting the scaling factor for the sediment transformation rate constant.

CONCLUSIONS

The application of the simulation method to experimental results found in literature for t-BPDP illustrates how LOTUS 1-2-3 programmed with QWASI improves the ability of the modeller to simulate experimental conditions by focussing on appropriate processes. This involves a systematic examination of the influence of various processes in the environment being modelled. The model is applicable to other organic chemicals and its simplicity allows it to run quickly on either personal (micro) or minicomputers.

A copy of the program which can be run in conjunction with LOTUS 1-2-3 on any IBM PC or IBM compatible, and a user's manual is available from Dr. Donald Mackay of the Department of Chemical Engineering and Applied Chemistry at the University of Toronto.

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EVALUATION OF SORBENT USE FOR RETRIEVAL OF SUNKEN HAZARDOUS LIQUIDS

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1 INTRODUCTION

The production and use of sorbents for spills clean-up is currently limited to oil and chemical spills on land and afloat on the water's surface. Discharge into water bodies, however, is not limited to chemicals that float on the water's surface, that dissolve or that are easily dispersed (nor is the eventual dispersion or dissolution of many of these chemicals necessarily desirable). Many of the chemicals having widespread industrial use, particularily the chlorinated hydrocarbons, are insoluble or only sparingly soluble in water, and as well have densities greater than that of water causing them to sink. These chemicals can be toxic to both humans and marine organisms. The increasing number of sunken insoluble chemical spills discovered in Canada has prompted the search for new technologies for recovery of chemicals from the bottoms of water bodies.

One of the methods currently being investigated at Environment Canada's Environmental Emergencies Technology Division is the use of sorbents to contain and retrieve these hazardous chemicals.

The most popular spill countermeasures presently being employed for sunken liquids are(1):

1) Capping and Burial-usually with clay,sand or diatomaceous earth.This method has the following disadvantages;the possibility of spreading the spill further;profound changes in the bottom topography destroying the local benthic organisms;and,that, after a period of time,leakage could occur recontaminating the surrounding area.

2) Suction Dredging-the most common technology in use and currently the most effective.The major disadvantage of this method is the requirement for on-site treatment of dredged materials.Water and solid material must be separated from the organic spill chemical and treated further before being returned to the environment. Furthermore,dredging may cause resuspension of the spilled chemical as well as disturbing bottom topography and benthic organisms.

This study examines the use of sorbents on sunken chemicals on a laboratory scale. Evaluation of all the parameters involved in the field use of sorbents (eg.weather and water conditions,etc.) is beyond the scope a laboratory study. However, this study will provide both a quantitative and a qualitative evaluation of the feasibility of sorbent use for sunken chemical spills recovery as well as point the direction for larger scale investigations.

Sorbents Tested

Previous EPS studies on sorbent use for floating spills (2,3,4,5) were used as a guide to the selection of sorbents that might be most successful in sunken chemical spills recovery. Sorbents were also selected to examine a variety of materials. The sorbents studied are shown in Table 1.

TABLE 1 SORBENTS TESTED

Sorbent Brand Name	Material of Construction
Graboil	treated polyurethane foam
Conwed-D	closed-cell polyethylene foam
Matasorb	polypropylene fabric
3-M Type 156 Pads	polyethylene fabric
Dow Imbiber Beads	cross-linked polymer beads
Conwed Pad	treated natural fibre reinforced with polypropylene mesh
Oclansorb	treated natural peat fibre
Granular Activated Carbon	type F-300 8*30

1.2 Study Parameters

The sorbents in this study were tested for ability to pick-up organic chemicals when brought into contact with them beneath the water's surface.

Six test liquids were chosen from EETD's list of priority pollutants.Two of these were reagent chemicals (1,2 dichloroethane and 1,2,4 trichlorobenzene), two household chemicals (creosote and latex) and two were authentic spill samples (perchloroethylene "puddle" material found in the St.Clair river near Sarnia,Ontario and coal tar found in the Rideau River in Ottawa,Ontario).

The following parameters were studied for each sorbent-liquid combination:

Sorbent Capacity (g test liquid/g sorbent): The amount of test liquid picked up by the sorbent after exposure.

Water Pick-up (% water by volume): Proportion of water picked up by sorbent during exposure to liquid in water.

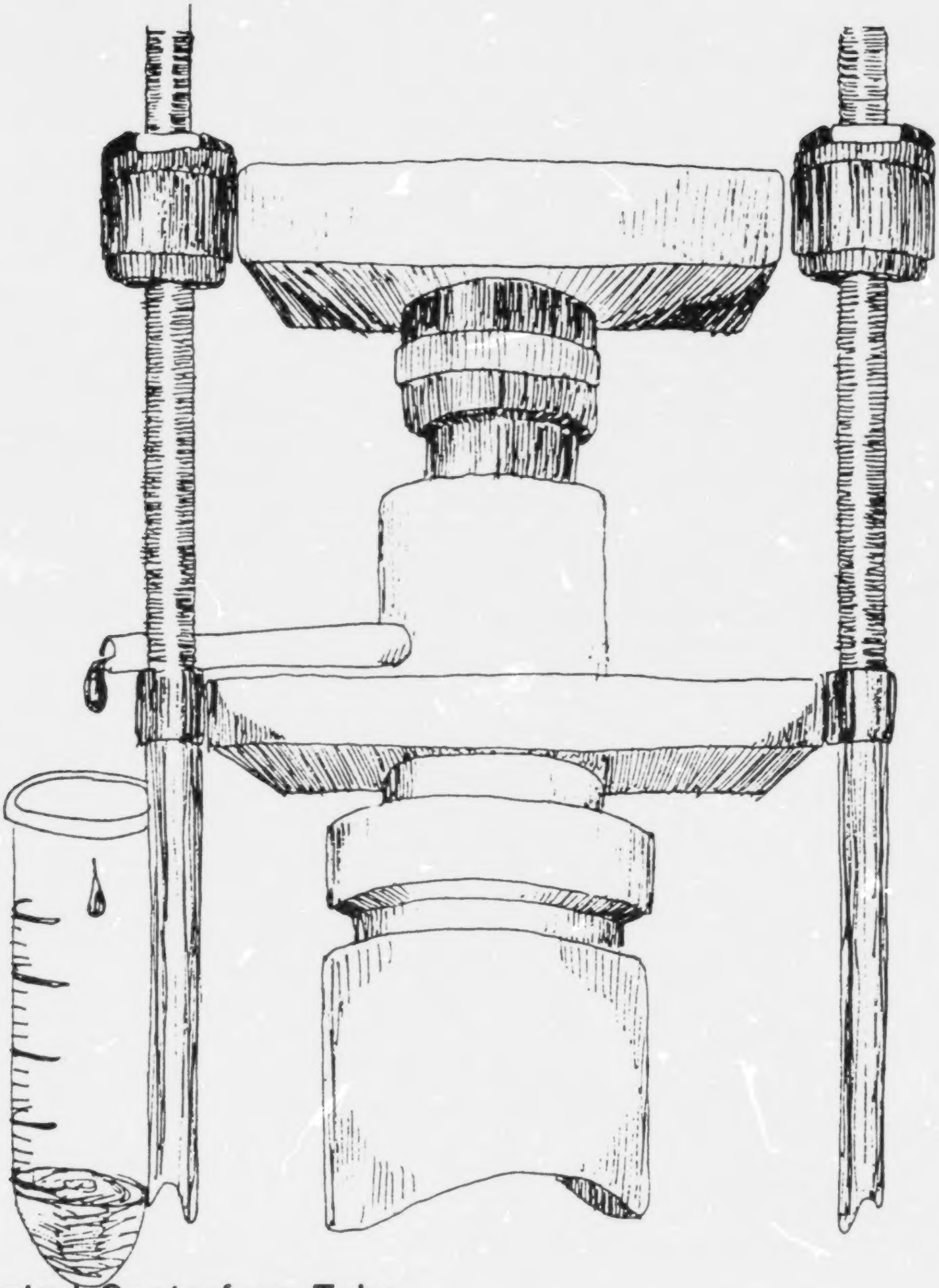
Reusability: The number of times the sorbent can be pressed and used again.

LABORATORY EVALUATION

The procedure used during this evaluation was developed from previous studies on sorbents (2,3,4,5,6) as well as the ASTM proposed standard methods for sorbent testing (ASTM F716-82).

Materials and Apparatus (see figures 1 and 2)

Standard laboratory glassware
Balance (Mettler P1200)
Carver Laboratory Press (Model B)
Squeezing Piston
Centrifuge (Fisher #37277H) with calibrated tubes
Viscometer (Brookfield Synchro-lectric Model LVT)
Reinforced glass tank (45 L)
Polypropylene tank (45 L)
2 Rotary Pumps (Cole Parmer, Model C-3250P)
Sorbents (see Table 1)-equipped with split-shot sinkers and fishing line guide-lines
-activated carbon was packaged in Tetley brand teabags
-Imbiber Beads were packaged in teabags made from the packaging of the large pads



raduated Centerfuge Tube

Figure 1: Hydraulic Press and Squeezing Piston

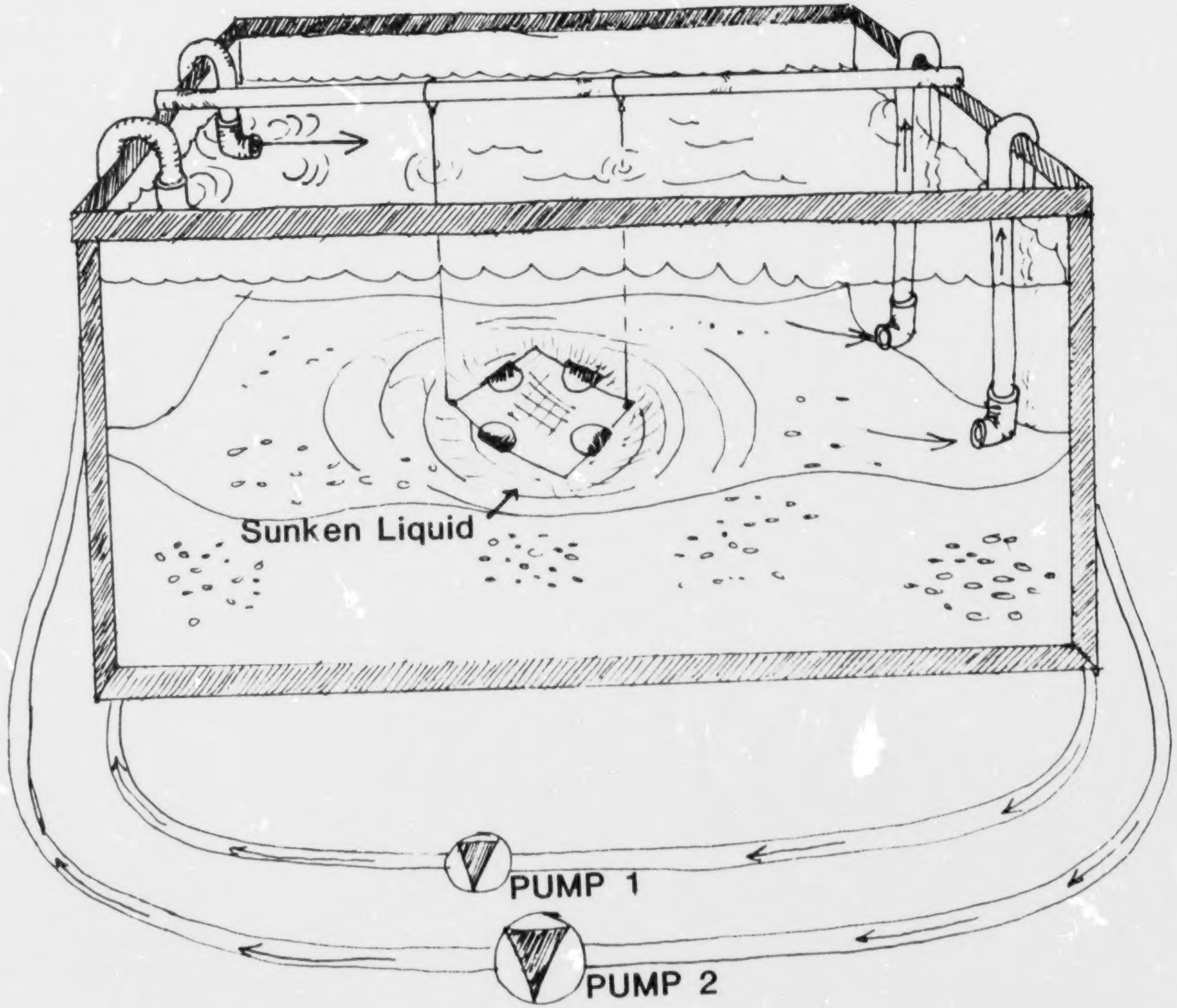

Sunken Liquid
PUMP 1
PUMP 2

Figure 2: Sunken Sorbent in Flowing Water System

Test Liquids:

1,2-Dichloroethane (Fisher Certified A.C.S)
1,2,4-Trichlorobenzene (Fisher HPLC Grade)
Creosote
Latex
Perchloroethylene "puddle" material from St.Clair River near Sarnia,Ontario.
Coal Tar from bottom of Rideau River in Ottawa,Ontario
Rideau River water
Tap water

Procedure

All test liquids were used as received with no subsequent treatment.

Red oil dye was used to colour those liquids that were colorless to render them more visible.

All samples were approximately 1g except the Imbiber Bead (2.5g) and activated carbon (5g) teabags. Viscosities were measured at 15 °C (except 1,2,4-trichloro-benzene which was measured at room temperature (26 °C) on a Brookfield viscometer. Densities were measured at room temperature (22 °C).

Evaluation of Sorbent Capacity in Test Liquid Alone

Each sorbent was preweighed,then submerged for one hour in enough liquid to completely cover the sorbent after saturation (preliminary testing showed that one hour was sufficient to saturate sorbents).

All liquids (except 1,2,4-trichlorobenzene) were brought to 10 °C before testing and maintained in a refrigerator at 10 °C during testing. 1,2,4-trichlorobenzene was tested at room temperature (22 °C) as this liquid solidifies at 17 °C.

After the one hour soak time the test sorbent was removed and allowed to drip until dripping slowed to 1 drop/15sec,then weighed.

Duplicate samples of each sorbent-liquid pair were run and if the two results were not within 10% of each other a third sample was tested.

Sorbent capacity in liquid alone was calculated as follows:

$$\text{Capacity} = \frac{\begin{array}{c}\text{(weight of test liquid}\\ \text{and sorbent after exposure)}\end{array} - \begin{array}{c}\text{(weight of sorbent}\\ \text{before exposure)}\end{array}}{\text{weight of sorbent before exposure}}$$

Sorbent Capacity for Test Liquid Sunk into Water

Duplicate samples of each sorbent were preweighed and sunk into the test chemical in water for one hour at 10°C. As in the first test(2.2.1), sufficient test liquid was added to the water to completely cover and saturate the sorbent. Following the sorption period the sorbent was retrieved and allowed to drip until the dripping had slowed to 1 drop/15 sec,then weighed.The sinkers were then removed from the sorbent and the liquid pressed from it at a maximum pressure of 3425 kPa (500psi). The pressed liquid was collected in a calibrated centrifuge tubes and centrifuged at medium setting for at least five minutes.

Following centrifugation, the volume of each separated liquid was measured.

After the pressing the sorbent was reweighed and returned, if possible, to the test liquid for reuse.This cycle was repeated until the sorbent capacity dropped to half the original capacity or the sorbent collapsed. A maximum of ten reuse tests were conducted for each sorbent.

As pressing was not possible for Imbiber Beads or activated carbon, water pick-up data from part 2.2.1 was used to estimate the water sorbed for these sorbents in the following manner:

Estimated mass of water sorbed (for activated carbon and Imbiber Beads) =

$$\text{sorbent capacity for water (g/g from 2.2.1)} * \text{sorbent weight}$$

Sorbent Capacity (for activated carbon and Imbiber Beads) =

$$\frac{\text{(weight of total liquid and sorbent after exposure)} - \text{(initial sorbent weight)} - \text{(estimated mass of water sorbed)}}{\text{initial sorbent weight}}$$

These calculations include the additional liquid sorbed by the packaging material. Activated carbon and Imbiber Beads have been shown by their manufacturers to have a preference for organic compounds over water and it is thus likely that the above estimations of water sorbed are greater than the true values.

For the remaining sorbents the Sorbent Capacity and Water pick-up were calculated in the following manner:

Assumption: Recovery of the liquid sorbed was not 100% but the assumption was made that the liquid remaining in the sorbent had the same composition as the liquid recovered.

In all calculations the density of water is not included as it is approximately equal to 1.0 at room temperature.

Sorbent Capacity = proportion by weight of test liquid sorbed * the total weight of liquid of liquid sorbed / weight of sorbent tested =

$$\frac{\text{\% test liquid sorbed (by volume)} \ast \text{density of test liquid}}{\text{\% test liquid sorbed} \ast \text{density of liquid} + \text{\% water pick-up}} \ast \frac{\text{(weight of test liquid, water, and sorbent after exposure)} - \text{(initial sorbent weight)}}{\text{initial sorbent weight}}$$

% Water Pick-up = $\dfrac{\text{water volume sorbed} \ast 100}{\text{total liquid volume sorbed}}$

Qualitative observations such as release of chemical into water during retrieval and integrity of the sorbent after use were also made.

Sorbent Capacity for Test Liquid in Flowing Water

To test and compare sorbent performance under flowing water conditions with a gravel bottom, a ten gallon glass aquarium was equipped with a flowing water system as shown in Figure 2.4. The tank was reinforced at the seams with silicone rubber caulking and silicone grease.

The flowrates for both pumps were set at 33 ml/sec bringing the total flowrate to 66 ml/sec and generating an observed current just beneath the surface of the water of approximately 14 cm/sec. The small size of the tank generated weaker currents in other areas as well.

Since the flowing water trials were conducted outdoors to provide adequate ventilation, the experimental temperatures could only be kept to 20°C - 25°C.

A depression was created in the gravel at the bottom of the tank and sufficient test liquid was added to more than saturate the sorbent.

As before, sorbents were exposed to the sunken liquid in water for one hour. As the sorbent was retrieved, it was moved across the outlets of the flow system to experience maximum current, at which point the sorbent was observed for release of chemical into the water.

The sorbent was treated after removal as in 2.2.2 with the following exceptions:

1) Since wind conditions could not be controlled and thus evaporation would be highly variable, the sorbent was only allowed to drip for approximately five seconds before being transferred into a closed weighing container.

2) Reusability was not tested during these trials.

The following sorbents were selected for testing in flowing water: Conwed, Conwed-D, Matasorb and Imbiber Beads. The following liquids were selected for the flowing water tests: 1,2-dichloroethane, St. Clair River perchloroethylene "puddle" material, and 1,2,4-trichlorobenzene.

When perchloroethylene was used as a test material, it was necessary to use a polyethylene test tank as the liquid was able to penetrate the seals in the glass tank.

The parameters measured were capacity and water pick-up.

Fate of Small Spill in Tank

To further test the feasibility of sorbent use, an amount of test liquid calculated to just saturate the sorbent tested was applied to the flowing water-gravel bottom tank as set up for 2.2.3. Following a five minute waiting period after liquid entry into the system the sorbent was applied and allowed to sorb for 30 minutes.

Volume of Liquid Applied =

$$\frac{\text{sorbent capacity} * \text{sorbent weight}}{\text{density of test liquid}}$$

The amount of test liquid recovered was determined by weighing and pressing. The percentage of test liquid recovered (by weight) was calculated as followed:

% Recovery = proportion of test liquid (by weight) * weight of liquid sorbed / weight of liquid applied

$$= 100 * \frac{\dfrac{(\%\text{ test liquid(vol)} * \text{density of test liquid})}{(\%\text{ test liquid} * \text{density of test liquid} + \%\text{ water}} * (\text{weight of sorbent, water, and test liquid after exposure}) - (\text{initial weight of sorbent})}{\text{weight of test liquid applied}}$$

RESULTS AND DISCUSSION

Overall results on all four tests indicate that synthetic sorbents have the greatest effectiveness against sunken organic chemicals,these sorbents having the highest capacity,lowest water pick-up, and greatest resistance to the destructive nature of the chemicals they sorb.

Release of chemicals back into the water upon retrieval is a major concern when recovering sunken liquids. Imbiber Beads showed the lowest observable release into the water, and the release appeared to come from the package rather than the beads. The synthetic fibre sorbents (Matasorb and 3-M) also showed lower release than the large-pore synthetic foam sorbents (Conwed-D and

Graboil). Graboil's release, in fact, was much greater than that of Conwed-D,particularly with the low viscosity chemicals.

The performance of the various sorbents depended much on the viscosities of the materials being recovered. The viscosities and densities of the test liquids are shown in Table 2.

Sorbent Performance in Test Liquid Alone

Table 3 shows the sorbent capacities in the test liquids alone.

In the more viscous test liquids (creosote,coal tar,and latex) the foam-type synthetic sorbents have much higher capacities .

In the less viscous test liquids, the synthetic fibre sorbents,as well as Conwed and Imbiber Beads, had capacities comparable but still not as high as the foam-type sorbents.

In all test liquids,the capacities of both Oclansorb and activated carbon are well below the other sorbents tested.

When water was used as a test solvent, all sorbents except Graboil and activated carbon demonstrated a hydrophobic nature.

Sorbent Performance on Test Chemicals Sunk into Water

Table 4 shows the sorbent capacity, water pick-up, and reusability for each sorbent-liquid pair, and Figures 3.1.1 to 3.6 illustrate these results.

Treated Natural Fibre Sorbents

Conwed sorbent pads exhibited high capacity for all the chemicals except for coal tar and latex. These liquids were too viscous to penetrate the fibre. Water pick-up for this sorbent was lower than all but 3-M and Matasorb. However, Conwed pads are not reuseable and do not posses the strength of the synthetic polymer sorbents. Performance of this sorbent was sufficient to continue testing in the flowing water trials.

Oclansorb exhibited a lower capacity for sunken organic chemicals than almost all other sorbents (except activated carbon), water pick-up was high,and this sorbent was not reuseable. Furthermore, the binding material dissolves in the chlorinated aliphatic solvents (1,2-dichloroethane and perchloroethylene) making recovery very difficult in these cases.

This sorbent was not tested further and is not recommended for sunken chemical spills recovery at this time.

Foamed Synthetic Polymer Sorbents

Conwed-D had a higher sorbent capacity for all liquids tested than all sorbents except Graboil. Water pick-up was not unacceptably high although it was higher than the synthetic fibre sorbents and Conwed. This sorbent is strong enough for maximum reuse and loses little of its capacity as it is reused. Conwed-D performed well enough to continue investigating its use.

Graboil, while having the highest capacity for all chemicals tested, had also the highest water pick-up showing little preference for organic chemicals over water.

While its reusability was high for most of the test liquids, strength deteriorated significantly on each reuse. Most importantly, Graboil's large release of chemical on retrieval and high water pick-up prevented it from being considered for further study.

Synthetic Polymer Fibre Sorbents

Both 3-M Type 156 Pads and Matasorb showed moderately high capacity for sunken chemicals compared to the other sorbents and had the lowest levels of water pick-up, in many cases less than 1%. 3-M is not as strong as Matasorb and thus not as reusable,both sorbents lost much of their capacity on reuse. Availability and greater strength made Matasorb the choice for the flowing water trial although 3-M has a greater capacity and should not be ruled out as a possible candidate for further study in sunken chemical spills recovery.

Cross-Linked Polymer Beads

Imbiber Beads had a lower capacity than the synthetic polymer sorbents and the polypropylene packaging material was not well penetrated by the higher viscosity test liquids. Futhermore, the beads cannot be pressed and reused. However these beads are highly hydrophobic and thus have low water pick-up. Most importantly, they do not release the sorbed material.

The versatility of the beads also made them a good candidate for further testing.

Granular Activated Carbon

The granular activated carbon used for this study was more dense than water and thus the easiest of the sorbents to sink. Large size (8 * 30) granular activated carbon was chosen for its easy packaging and to minimize suspension of carbon dust particles in the water. However,as well as having the lowest capacity of all the sorbents tested for every test liquid, the activated carbon released a great deal of dust into the water, which, in the field, could cause respiratory problems for aquatic organisms. This sorbent was not tested further.

Effect of Flowing Water on Sorbent Performance

The effects of flowing water on the capacity and water pick-up of Matasorb, Conwed, Conwed-D, and Imbiber Beads for the test liquids 1,2-dichloroethane, perchloroethylene "puddle", and 1,2,4-trichlorobenzene are shown in Table 5.

For most sorbent-liquid pairs there were few significant changes in capacity. The small measured gains in capacity of some sorbents could be due to the shorter drip time during testing, lowered viscosity of the liquids as a result of warmer temperatures, and facilitation of pick-up by local currents.

The Imbiber Bead-1,2-dichloroethane and Imbiber Bead-perchloroethylene pairs showed significant losses in capacity although there was no apparent increases in water pick-up when exposed to flowing water and a gravel bottom. The reasons for this are not clear as the sorbent did not release significant amounts of liquid on retrieval.

Only small increases in water pick-up were observed for the other sorbents, with Matasorb performing the best at no significant increase.

Conwed-D had the highest increase, at 29%, over the stagnant water tests when sorbing perchloroethylene "puddle" material. At this level water pick-up is already a significant factor and may increase further when exposed to a greater current.

The water pick-up for Conwed also increased slightly but this may be due to deterioration of the hydrophobic treatment chemical of the pad evident at this stage of testing.

Fate of Small Spills in Tank

This test was performed to gain insight into how much of a spill can actually be recovered by sorbents. The results shown in Table 6 reflect not only the sorbent's ability to sorb from the gravel bottom, but the test liquid's ability to penetrate it. As well there may be losses of spilled test liquid due to dispersion and evaporation.

Perchloroethylene completely penetrated the gravel bottom, thus making contact with the sorbents impossible. Penetration of the bottom material will greatly depend on the natures of both the bottom and the sunken liquid.

Results for Conwed pads are incomplete as the pads were no longer usable at this point in the testing. This may be due to deterioration of the treatment material, possibly because of the high summer temperatures.

Matasorb, Conwed-D, and Imbiber Beads all showed good pick-up of 1,2-dichloroethane and 1,2,4-trichlorobenzene. Matasorb demonstrated the highest recovery at an average of 78% liquid recovery. It is possible the pick-up is greatest for Matasorb because this sorbent is the least rigid of the sorbents tested, while the Imbiber Bead packet, the most rigid, had the lowest pick-up. A stiff sorbent would be less able to contact well with an uneven surface,such as those found on the bottoms of lakes and rivers.

CONCLUSIONS

Sorbent use for recovery of sunken hazardous chemical spills shows sufficient promise to be studied further.

Polypropylene and polyethylene synthetic polymer sorbents, as well as cross-linked polymer beads, were the most successful sorbents tested in this study. These sorbents exhibited high capacity, low water pick-up, and little release of sorbed chemical on retrieval.

Polyurethane, treated organic fibre and activated carbon sorbents have various shortcomings that don't recommend them to use for sunken chemicals recovery.

The performances of those sorbents tested in flowing water (Conwed, Matasorb,Conwed-D, and Imbiber Beads) were not adversely affected to a significant degree by the low current in which they were tested.

RECOMMENDATIONS

Study should be continued on a larger scale with simulated field conditions that include variations in current velocity, water depth, and wave height.

A method of physically measuring release of sorbed material into water by sorbents during retrieval should be developed for further testing.

Other synthetic materials (polyester,polyether etc.)should be examined in future.

A greater variety of deployment methods should be developed and studied.

ACKNOWLEDGEMENTS

A sample of the coal tar found at the bottom of the Rideau River in Ottawa was provided by Integrated Explorations while working with Proctor and Redfern.

Perchloroethylene "puddle" material from the bottom of the St.Clair River near Sarnia,Ontario was provided by Dow Chemicals of Canada.

The sorbents were provided by their respective manufacturers and distributors.

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TABLE 2 VISCOSITY AND DENSITY OF TEST LIQUIDS

Test Liquid	Viscosity (mPa.s)	Density (g/ml)
1,2-dichloroethane	0.89	1.25
perchloroethylene	0.93	1.60
1,2,4-trichlorobenzene	2.4 @ 26°C	1.45
creosote	23	1.01
coal tar	4600	1.07
latex*	/	1.2

*viscosity not available

TABLE 3 SORBENT CAPACITY IN TEST LIQUID ALONE (g/g)

SOLVENT	Conwed	Oclan-sorb	Graboil	Conwed D	Mata-sorb	3-M	Imbiber Beads	Act. Carbon
Water	0.6	1.1	19	2.2	0.6	0.4	1.2	1.3
1,2-dichloro-ethane	11.3	3.8	22.5	13.9	10.1	13.7	7.7	1.1
Perchloro-ethylene	13.7	5.7	33	27	14	18	10	1.5
1,2,4-Tri-chloro-benzene	14.4	4.4	21	23	12.1	14.0	12.1	1.3
Creosote	10.0	2.9	29	18.8	8.2	10.1	3.8	1.1
Coal Tar	*	3.7	52	32	13	17	**	**
Latex	**	**	26	40	**	**	**	**

* sorbent collapsed durring retrieval

** test liquid did not completely penetrate sorbent

TABLE 4: SORBENT CAPACITY, WATER PICK-UP, AND REUSABILITY IN WATER

TEST LIQUID	SORBENT	SORBENT CAPACITY(g/g)	% WATER PICK-UP	REUSES
1,2-dichloro-ethane	Conwed	12.0	3	0
	Oclansorb	cp	-	-
	3M 156	12.4	2	4
	Matasorb	8.8	9	8
	Conwed-D	13.6	15	8
	Graboil	21.1	25	3
	I.Beads*	7.4	na	0
	GAC*	1.9	na	0
Perchoro-ethylene "puddle"	Conwed	15.9	11	0
	Oclansorb	2.8	73	0
	3M 156	18	12	2
	Matasorb	14.2	8	5
	Conwed-D	24.3	38	10
	I.Beads	10.8	na	0
	GAC	2	na	0
1,2,4-trichloro benzene	Conwed	11.5	21.0	0
	Oclansorb	2.9	64	0
	3M 156	14.7	12	2
	Matasorb	11.4	3	4
	Conwed-D	19.9	17	10
	Graboil	23.2	33	8
	I.Beads	6.1	na	0
	GAC	1.6	na	0
Creosote	Conwed	10.2	1	0
	Oclansorb	3.4	1	0
	3M 156	12.1	1	2
	Matasorb	8.2	1	10
	Conwed-D	14.9	9	10
	Graboil	19.5	17	10
	I.Beads	4.1	na	0
	GAC	1.6	na	0
Coal Tar	Conwed	cp	-	-
	Oclansorb	2.1	32	0
	3M 156	17.5	2	0
	Matasorb	13.2	1	3
	Conwed-D	16.9	28	3
	Graboil	41.4	22	1
	I.Beads	np	-	-
	GAC	np	-	-
Latex**	Conwed-D	18.0	na	10
	Graboil	30	na	10

* capacity includes that of the sorbent packaging
**only Conwed-D and Graboil penetrated
cp-sorbent collapsed   np-sorbent not penetrated
na-not applicable

TABLE 5 COMPARISON OF SORBENT CAPACITY AND WATER PICK-UP, IN STAGNANT AND FLOWING WATER

SORBENT	LIQUID	SORBENT CAPACITY STAG. WATER (g/g)	SORBENT CAPACITY FLOW. WATER (g/g)	% WATER PICK-UP STAG. WATER	% WATER PICK-UP FLOW. WATER	CHANGE IN FLOWING WATER CAPACITY	CHANGE IN FLOWING WATER % PICK-UP
MATASORB	ED	8.8	9.7	9.0	4.0	+10%	-5%
	PERC	14.2	14.7	8.0	10.0	+4%	+2%
	1,2,4-TCB	11.4	12.4	3.0	4.0	+9%	+1%
CONWED	ED	12.0	11.2	3.0	18.0	-7%	+15%
	PERC	15.9	13.4	11.0	19.0	-16%	+8%
	1,2,4-TCB	11.5	14.1	21.0	13.0	+23%	-8%
CONWED-D	ED	13.6	13.7	15.0	15.0	+1%	0%
	PERC	24.3	20.9	9.0	38.0	-14%	+29%
	1,2,4-TCB	19.9	20.8	8.0	17.0	+5%	+9%
IMBIBER BEADS	ED	7.4	5.4	na	na	-27%	na
	PERC	10.8	7.9	na	na	-27%	na
	1,2,4-TCB	6.1	6.1	na	na	0%	na

ED ; ethylene dichloride
PERC ; perchloroethylene
1,2,4-TCB ; 1,2,4,-trichlorobenzene

TABLE 6 FATE OF SMALL SPILL IN TANK

Test Liquid	Sorbent	% Recovery
1,2-dichloroethane	Matasorb	73
	Conwed	**
	Conwed-D	65
	Imbiber Beads	69
Perchloroethylene	Matasorb	<1
	Conwed	**
	Conwed-D	<1
	Imbiber Beads	<1
1,2,4-trichlorobenzene	Matasorb	83
	Conwed	**
	Conwed-D	75
	Imbiber Beads	64

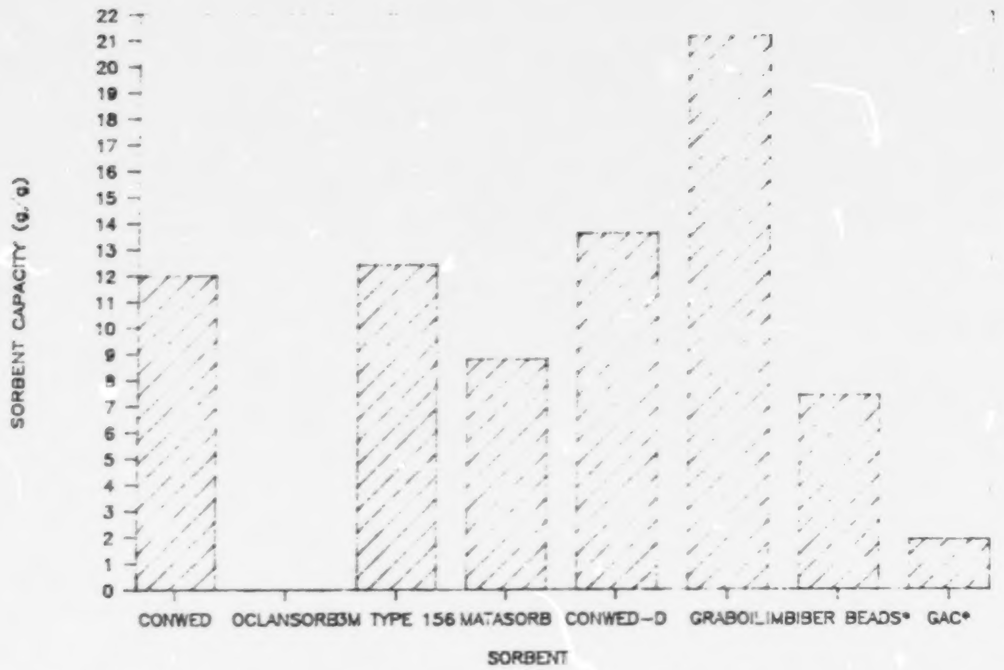

FIGURE **3.1.1** Sorbent Capacity in 1,2-Dichloroethane and Water

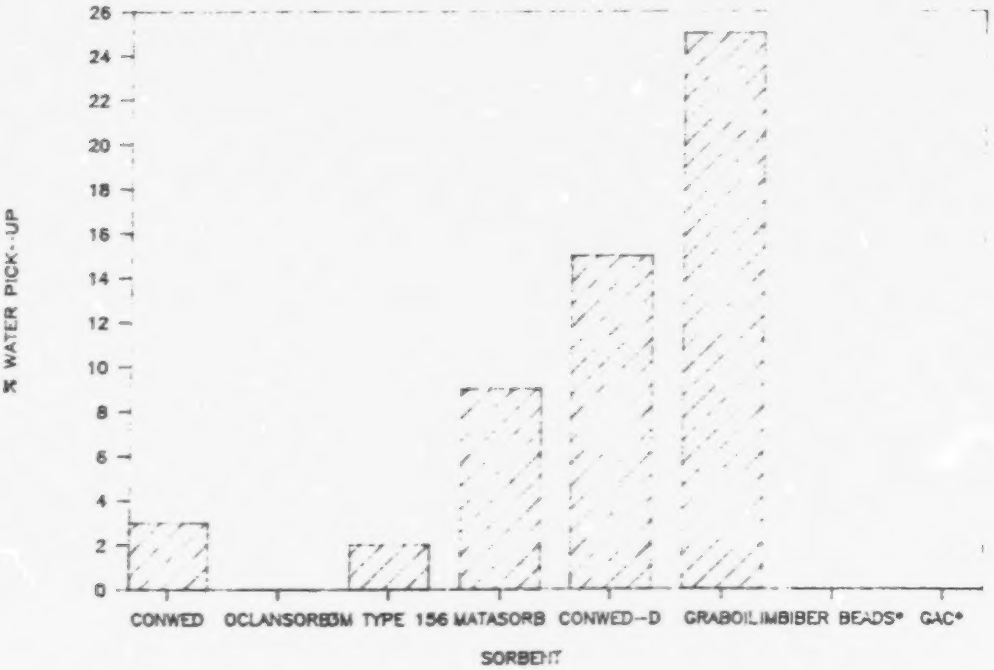

FIGURE **3.1.2** Water Pick-up in 1,2-Dichloroethane and Water

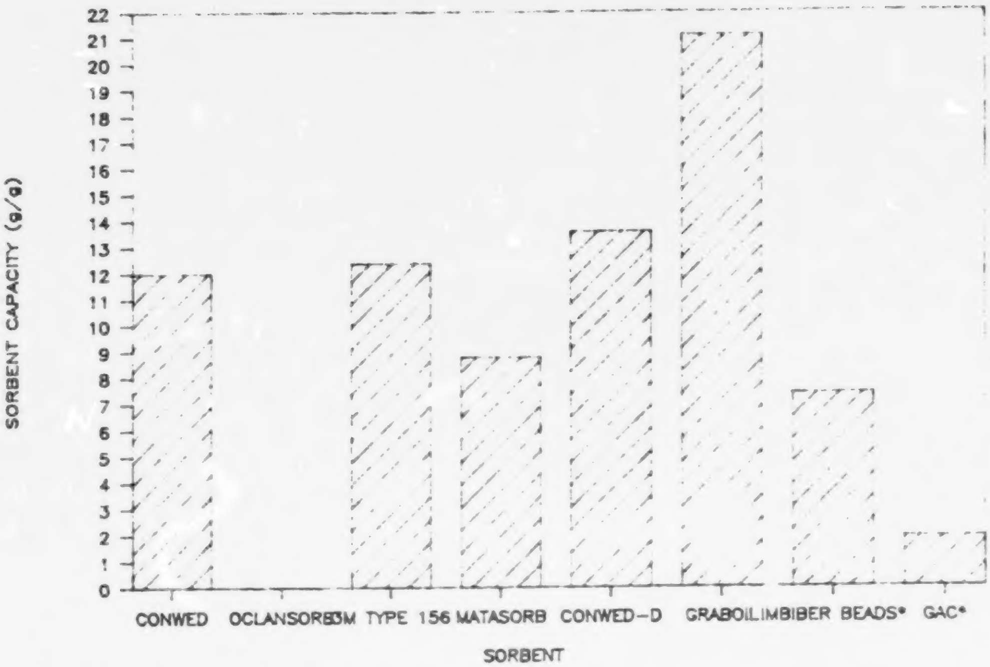

FIGURE **3.2.1** Sorbent Capacity in Perchloroethylene "Puddle" and Water

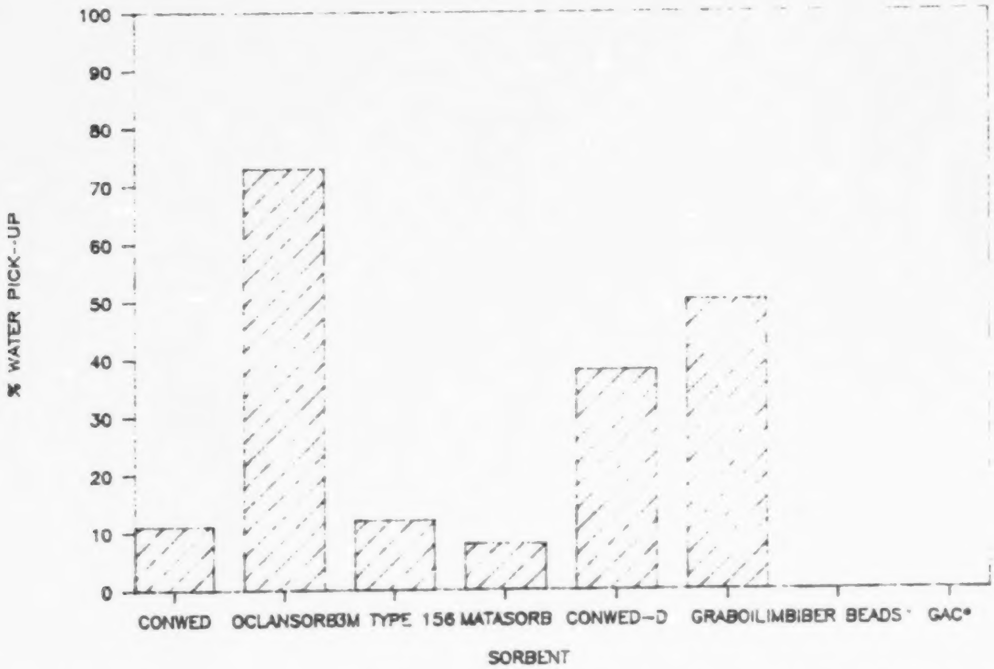

FIGURE **3.2.2** Water Pick-up in Perchloroethylene "Puddle" and Water

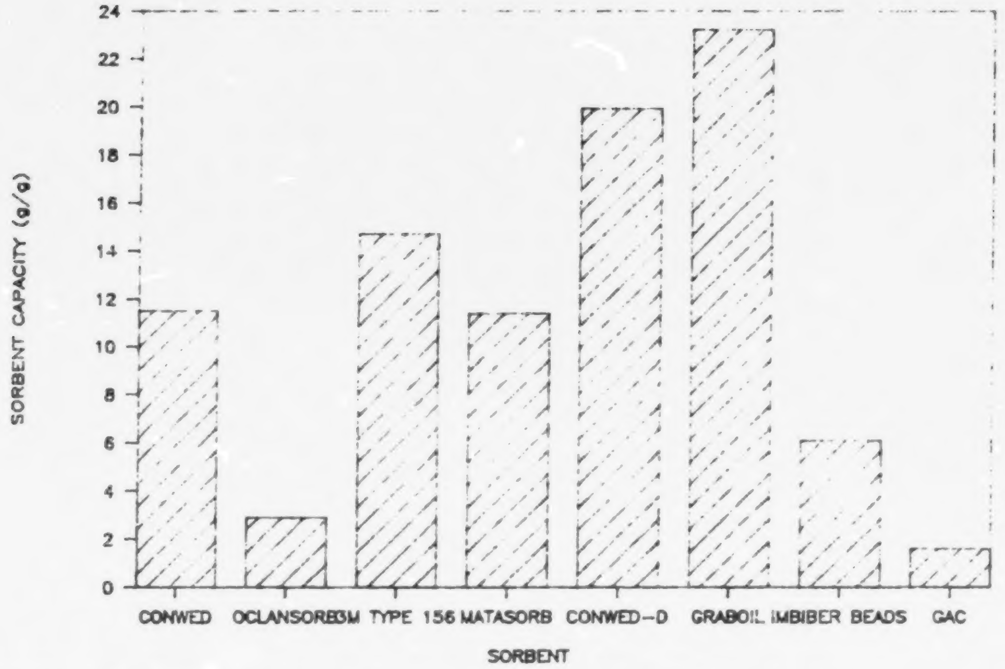

FIGURE 3.3.1 Sorbent Capacity in 1,2,4-Trichlorobenzene and Water

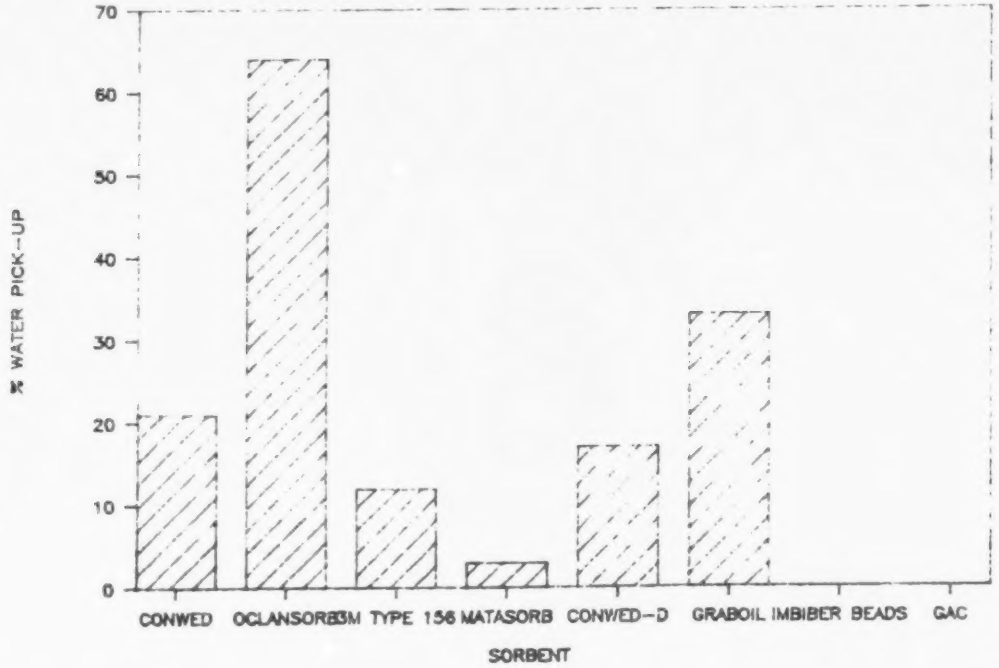

FIGURE 3.3.2 Water Pick-up in 1,2,4-Trichlorobenzene and Water

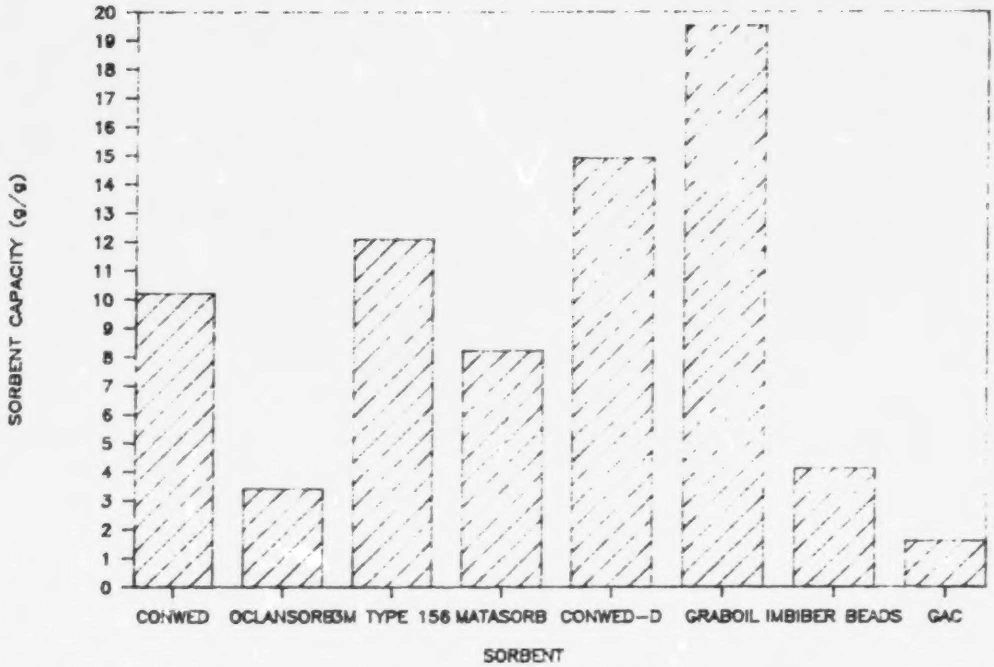

FIGURE **3.4.1** Sorbent Capacity in Creosote and Water

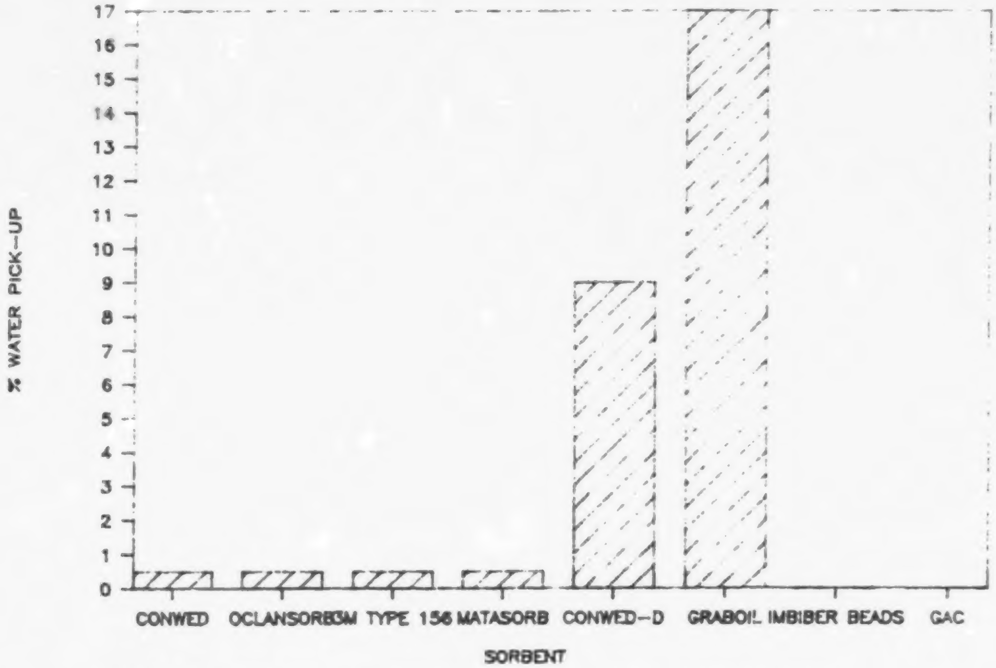

FIGURE **3.4.2** Water Pick-up in Creosote and Water

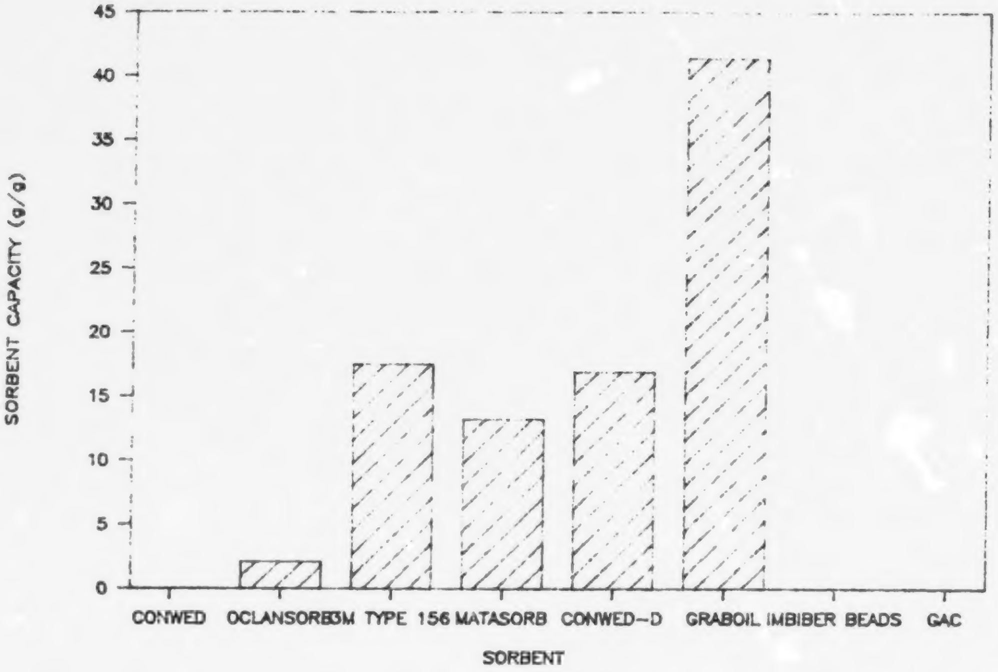

FIGURE **3.5.1** Sorbent Capacity in Coal Tar and Water

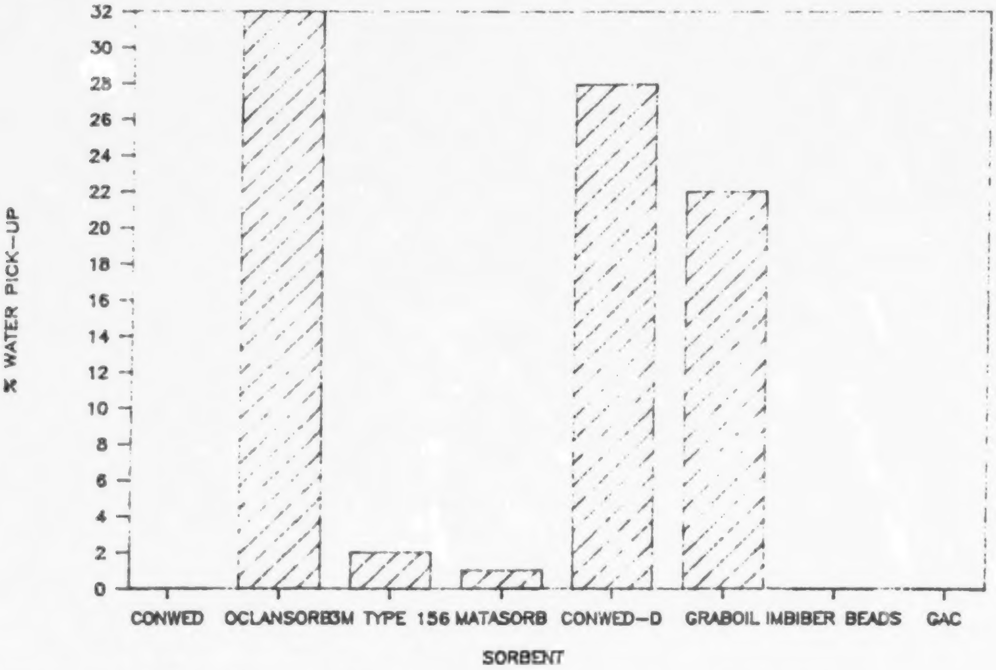

FIGURE **3.5.2** Water Pick-up in Coal Tar and Water

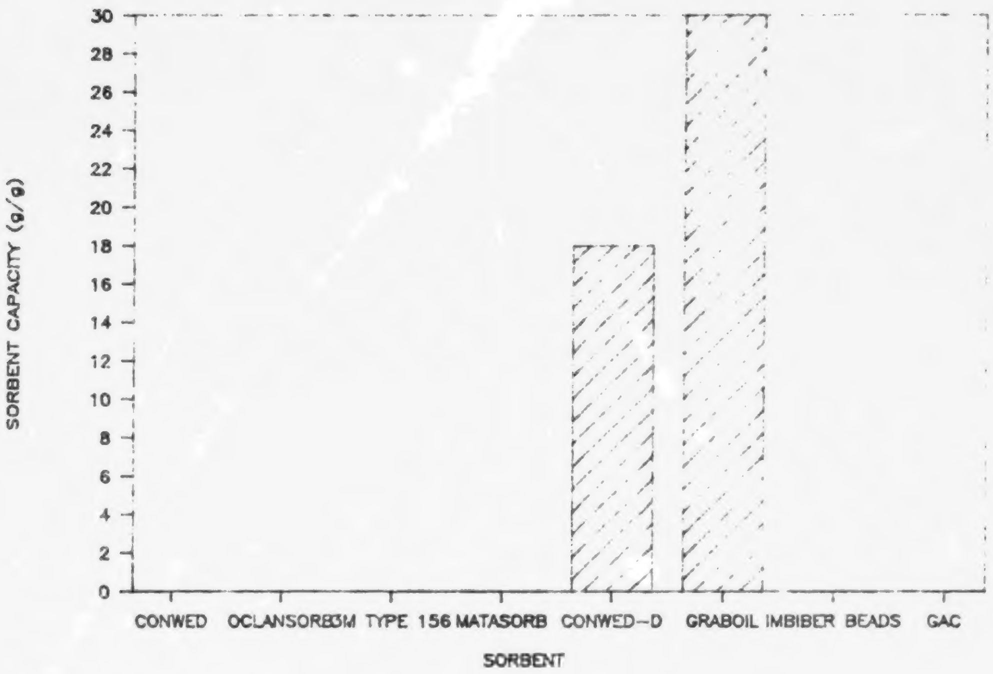

FIGURE **3.6** Sorbent Capacity in Latex and Water

RECLAMATION OF DISPERSED BRINE SPILL SITES IN SEMI ARID CLIMATES

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ABSTRACT

A study of different reclamation procedures to determine the most effective one has been conducted on a brine contaminated mineral soil in southeastern Saskatchewan. A total of 10 test zones were established in order to evaluate 9 soil amendment programs. Salt removal was measured by soil sampling to a maximum depth of 0.6 metres. A reclamation program is outlined which recommends reclaiming these sites with gypsum, manure and ammonium nitrate. The effectiveness of the program can be enhanced by soil ripping and flushing.

INTRODUCTION

Brine is often produced with crude oil and must be separated from it at a processing facility prior to disposal by deep well injection. As oil producing fields decline in productivity, larger volumes of salt water are produced. This trend has led to higher pipeline pressures and corrosion rates and has resulted in an increasing frequency of salt-water spills. In response to this situation, companies have developed spill clean-up programs with a variety of soil reclamation techniques designed to meet the needs of a number of soil and climatic conditions. To date little data has been collected for semi-arid areas such as southeastern Saskatchewan in which a number of old producing fields are located.

There are two primary affects of brine on soil fertility. Both the physical structure of the soil and the normal osmotic gradient existing between plant roots and soil are altered.

The soil structure is sensitive to high NaCl concentrations because clay particles have an absorption shell about them which behaves like an ion exchange medium. Calcium and magnesium ions are normally bound to these shells but are displaced by sodium when a brine spill occurs. After a rainfall, the calcium and magnesium ions are washed away allowing the absorption shells to swell. The swelling leads to structural breakdown of the soil and constriction of soil spaces (Richards et al 1969). This phenomena is known as dispersion. When a dispersed soil dries out it hardens into an impenetrable mass that inhibits gas and water exchange with plant roots.

High concentrations of NaCl can also reverse the normal osmotic gradient that exists between soil and plant roots (Henry et al. 1979). This gradient is responsible for the transfer of water and nutrients from the soil to the plant. After a spill, vegetation quickly dies from dehydration and nutrient deficiencies.

Reclamation of contaminated sites traditionally consists of incorporating a calcium source, a fertilizer and an organic amendment such as manure into the top soil (de Jong 1977). Rainfall is relied upon to leach the calcium down into the deeper soil layers and to flush the displaced sodium out of the root zone. The role of the organic amendment is primarily to maintain soil permeability. The fertilizer promotes new vegetation growth.

The climate and soils of southeastern Saskatchewan represent a particularly difficult reclamation problem. Low rainfall, shallow ground water and high evaporation rates combine to concentrate salt at the soil surface and maintain it there indefinitely. The soils of this area are often high in clay content and consequently they disperse easily. Many of these soils support some type of agriculture and so an effective reclamation program is needed.

OBJECTIVE

The objective of this study was to examine amendments and procedures to reclaim brine affected soils in semi-arid climates. The approach was to conduct a set of field trials to:

a.) compare the relative effectiveness of gypsum to Saline Soil Saver (SSS) as an amending source of calcium. SSS is a commercially available product (Bondell Group of Calgary Alberta) that contains calcium nitrate in solution. It has not been used to reclaim dispersed brine affected sites in the area before.

b.) evaluate the effectiveness of flushing a calcium amended site.

c.) evaluate the possible benefits of soil ripping on salt removal.

SAMPLING METHODOLOGY

Soil amendment performance was measured by soil sampling. Soil samples were collected with a Dutch Auger at three sampling depths, 0-20 cm, 20-40 cm, 40-60 cm. A composite sample was obtained by combining three random samples per depth from each of the three plots in a given treatment zone. The resulting three analyses per depth for each zone were averaged to give one analysis per depth for each zone.

SITE DESCRIPTION

The chosen site is shown in figure 1 and was selected primarily because it had good drainage. It was located approximately 200 km south east of Regina Saskatchewan. The presence of a service road made the location easily accessible and because it was at the edge of a cropped field studies could be carried out with minimal interference to the adjacent farming operations. The surface terrain was essentially level with a slight slope to the west.

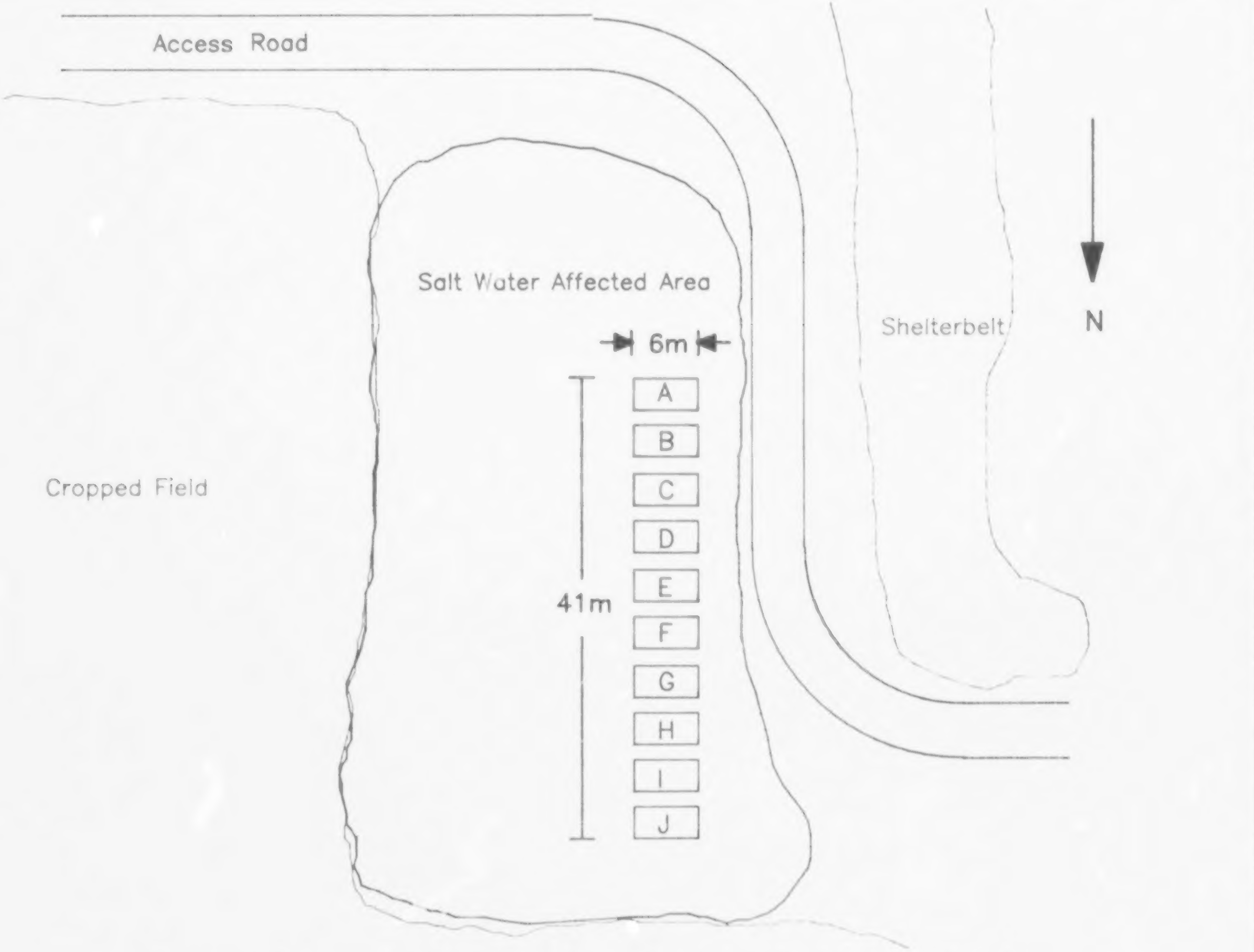
Access Road
Salt Water Affected Area
Shelterbelt
N
6m
A
B
C
D
E
F
G
H
I
J
41m
Cropped Field

Figure 1 Schematic Diagram of the Steelman 9–14–4–6W2 Brine Reclamation Test Site, May 1986

Ten test zones were staked out and labelled A through J. Each zone was 6 m long and 3 m wide and was separated from the next zone by a 1.2 m buffer strip. Each zone was subdivided into 3 test plots from which soil samples were taken. The plots were 1.2 m square with 0.6 m buffer strips.

CALCIUM AMENDMENT PERFORMANCE EVALUATION

Procedure The relative abilities of gypsum and SSS to remove sodium from the soil were evaluated by comparing the salt removal performance of gypsum and SSS treated test zones to a control. To do this most effectively the zones E and F were selected for the comparison because they had very similar sodium concentration profiles and because they lay beside each other so that their soil composition was as similar as possible. Equivalent quantities of available calcium and nitrogen were calculated for both the amendment cases applied.

Gypsum is the traditional calcium source for reclamation because it is cheap and easily available. Saline Soil Saver is more expensive but it is a liquid which makes the calcium more readily available to the soil. It is also recognized that a liquid amendment is easier to store and apply, especially in difficult terrain. Saline Soil Saver contains nitrogen as well as calcium and so fertilizer requirements are not as high with this product as they would be with gypsum. It contains a proprietary polymeric wetting agent designed for maintaining soil spaces once the calcium has reduced the size of the clay particles. This would help prevent redispersion once reclamation has begun.

The amendments that were applied in May 1986 are presented in Table 1. The control case is represented by Zone D. The SSS treated zone is E and the gypsum treated one is F. Both of the amended zones were rototilled to a depth of 23 cm to improve amendment contact with the soil.

The data for this study was collected in May 1986 and October 1986. Analysis of the results was based on 3 key parameters. They were the change in soluble sodium concentration, percent change in soil electrical conductivity (EC) and percent change in sodium adsorption ratio (SAR). These parameters reflect the removal of sodium from the soil and can be used for comparative purposes.

Results and Discussion The May 1986 soil analysis indicated that the top soil was 20-25 cm of clay loam underlain by heavy clay. Initial sodium concentrations (measured in milliequivalents/litre) in the three 20 cm layers were, from top to bottom: 318 meq/l, 252 meq/l, 226 meq/l. The higher surface salt concentrations indicated that evaporation was taking place due to insufficient rainfall.

Results presented in Table 2 give the percent change in the key parameters that occurred between May and October 1986. The data for the control zone (D) indicates that an increase in sodium levels at the soil surface occurred during the study period and that sodium migrated from the lower soil depths. Probably, evaporation of moisture from the soil surface concentrated salts within the uppermost soil layer. Sodium levels decreased in both of the treated zones. Gypsum and SSS treatments removed equivalent amounts of salt at the soil surface but SSS has shown slightly superior performance deeper down. This is evident that because the calcium in the SSS is in a more available form it can penetrate through the soil more easily than the calcium in the gypsum.

ZONE	AMENDMENT	APPLICATION RATE	APPLICATION METHOD
D	no additive	no additive	no additive
E	Manure SSS	10 cm Thickness 29.5 drum/ha	Back hoe + frontend loader pressurized sprayer and perforated bucket
F	Manure Gypsum Ammonium Nitrate	10 cm thickness 21.5 tonne/ha 0.735 tonne/ha	backhoe & frontend loader By hand and hand-held broad caster By hand

TABLE 1 AMENDMENT APPLICATIONS USED IN THE CALCIUM AMENDMENT PERFORMANCE EVALUATION, MAY 1986

ZONE	SOIL DEPTH IN CM	Na %	EC %	SAR %
Control (D)	0-20	18.5	13.2	1.9
	20-40	-42.7	-40.2	-6.5
	40-60	-42.6	-38.4	-2.4
SSS (E)	0-20	-68.4	-49.8	-58.2
	20-40	-27.2	-15.6	-28.0
	40-60	-11.5	-2.7	-20.5
Gypsum (F)	0-20	-64.4	-49.2	-55.3
	20-40	-19.7	-16.5	-16.1
	40-60	6.5	1.4	3.3

TABLE 2 RESULTS OF THE 1986 GYPSUM/SSS PERFORMANCE EVALUATION SHOWING PERCENT CHANGE IN KEY PARAMETERS

FLUSHING ASSESSMENT

Procedure The effectiveness of flushing a calcium amended soil was evaluated by comparing the performance of non-flushed treatment zones with identically treated flushed ones. Flushing was carried out in July/August 1986 as well as July/August 1987.

In 1986 a total of 5.5 m3 (75 mm of irrigation per zone) of flush water was applied in two equal treatments to the gypsum amended zone, G, and the SSS amended zones, H, I and J. Zone G was amended identically to zone F and zones H,I and J were amended similarly to zone E. Water was sprayed onto the zones from a water truck. About 50% ran off the zone surfaces and even distribution was difficult to achieve.

In June 1987 a portable irrigation unit was designed and installed so that flush water run off and distribution could be improved. It is illustrated in Figure 2. Run off was reduced by providing lower flow rates than in 1986 which improved water absorption by the soil. Better distribution across the zone surfaces was also achieved by using soaker hoses to spray water evenly over each zone surface. Water flow to each hose was controlled by a valve that connected the hosing to the distribution header. A total of 13.5 m3 (182mm of irrigation per zone) of flush water was supplied to four zones using this unit.

The zones flushed in 1987 were A, C, G and I. Zones A and C were ripped and will be discussed in the ripping assessment. Zones G and I were again flushed in 1987 to provide data over two growing seasons.

Results and Discussion Results from the 1986 flushing are presented in Table 3 and may be compared to those obtained for the non flushed case in Table 2. In general, both SSS and gypsum removed more salt when flushed. The only exception to this occurred in the upper most layer of zones I and J. These zones did not perform as well as zone E probably because their initial salt concentrations were significantly lower than the initial zone E levels.

Results from the 1987 flushing are presented in Table 4. By comparing the results from the non-flushed zones E and F to the flushed zones G and I it can be seen that again flushing has significantly improved salt removal rates. In fact, zones E and F experienced an increase in sodium levels that was more extreme in the shallower depths. This is probably the result of surface evaporation bringing salts towards the surface.

It appears that flushing maintains a net downward flow of salts through the soil profile.

RIPPING ASSESSMENT

Procedure The zones A, B and C were ripped to a depth of 75 cm with a one shank ripper mounted on a backhoe. Amendments, application rates and application methods are given in Table 5. Zone A was amended identically to zone F and zone B was amended in the same manner as zone E. Zone C was amended similarly to zone F except that straw was used instead of manure. The amount of straw used closely approximates the manure loading used on F.

Both zones A and C were flushed in 1987.

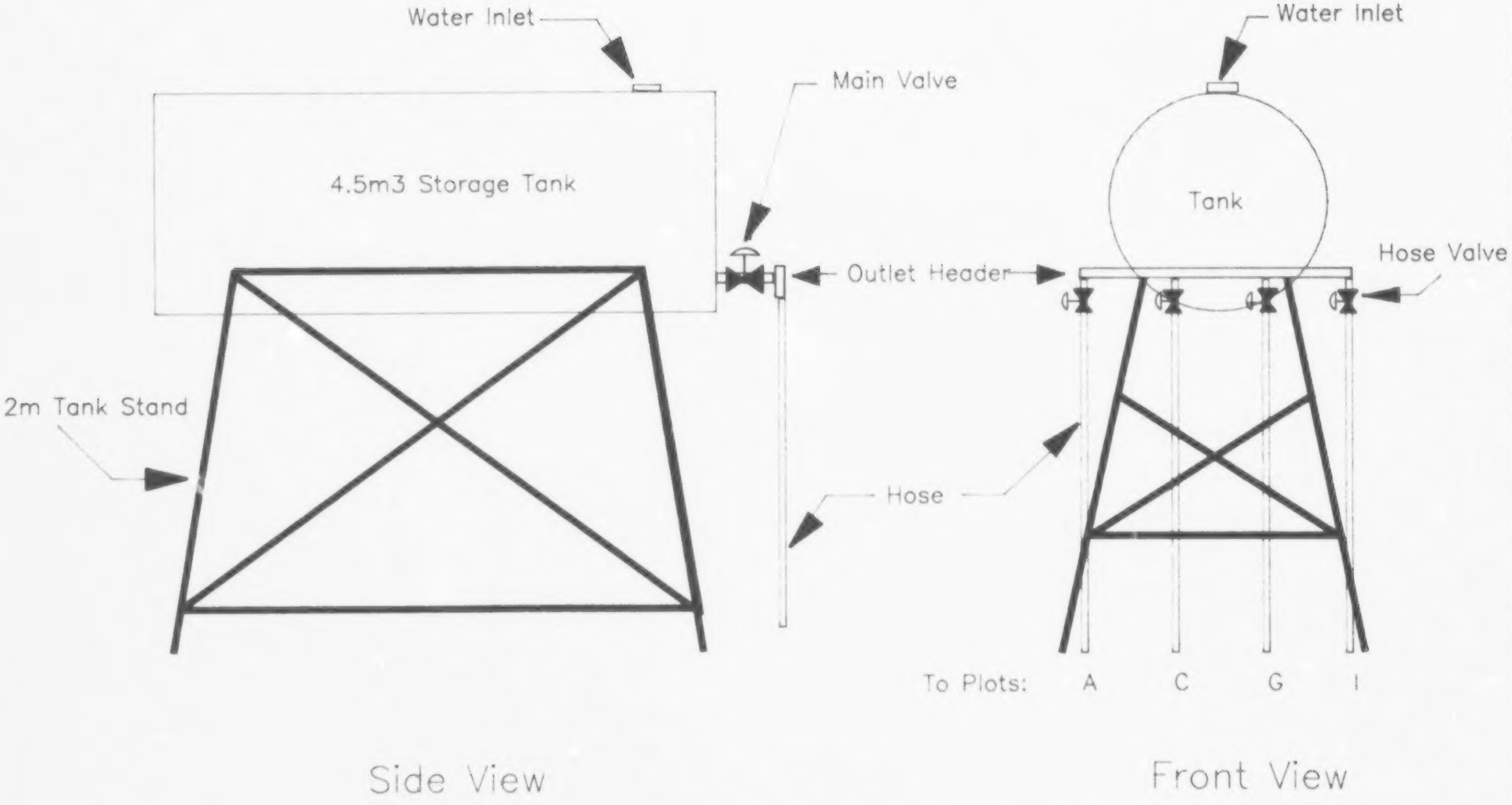
Water Inlet
4.5m3 Storage Tank
2m Tank Stand
Main Valve
Outlet Header
Hose
Water Inlet
Tank
Hose Valve
To Plots: A C G I
Side View
Front View

Figure 2 Schematic Diagram of Portable Irrigation System Used During May87–September87 at Steelman 9–14–4–6W2

ZONE	SOIL DEPTH IN CM	Na %	EC %	SAR %
G (flushed/ gypsum)	0-20	-70.8	-43.9	-65.8
	20-40	-48.3	-18.5	-46.8
	40-60	-39.6	-10.0	-34.8
H (flushed/ SSS)	0-20	-65.5	-27.6	-57.6
	20-40	-58.3	-23.8	-55.1
	40-60	-47.3	-14.2	-45.3
I (flushed/ SSS)	0-20	-29.0	-46.2	-42.1
	20-40	-38.6	-3.7	-45.3
	40-60	-38.3	2.6	-43.4
J (flushed/ SSS)	40-20	-49.3	-18.6	-49.9
	20-40	-36.0	-21.9	-40.8
	40-60	-28.8	-18.3	-28.5

TABLE 3 RESULTS OF THE 1986 FLUSHING ASSESSMENT PROGRAM SHOWING PERCENT CHANGE IN KEY PARAMETERS

ZONE	SOIL DEPTH IN CM	Na %	EC %	SAR %
G (flushed/ gypsum)	0-20	-2.8	-4.4	-8.5
	20-40	-4.9	-8.3	-11.3
	40-60	-11.2	-15.4	-19.6
I (flushed/ SSS)	0-20	-13.6	-41.5	-4.3
	20-40	-0.3	-7.7	-5.4
	40-60	3.2	-0.4	-6.8
F (gypsum)	0-20	6.6	4.4	9.0
	20-40	2.0	0.4	2.7
	40-60	3.0	-2.0	1.6
E (SSS)	0-20	6.1	6.1	8.3
	20-40	6.3	7.5	4.6
	40-60	-1.1	-1.7	-4.8

TABLE 4 RESULTS OF THE 1987 FLUSHING ASSESSMENT PROGRAM SHOWING PERCENT CHANGE IN KEY PARAMETERS

ZONE	AMENDMENT	APPLICATION RATE	APPLICATION METHOD
A	Manure Gypsum Ammonium Nitrate	10 cm thickness 21.5 tonne/ha 0.735 tonne/ha	backhoe & frontend loader By hand and hand-held broad caster By hand
B	Manure SSS	10 cm Thickness 29.5 drum/ha	Back hoe + frontend loader pressurized sprayer and perforated bucket
C	Straw Gypsum Ammonium Nitrate	4 Bales straw 21.5 tonne/ha 0.735 tonne/ha	By hand By hand and hand-held broad caster By hand

TABLE 5 AMENDMENT APPLICATIONS USED IN THE RIPPING ASSESSMENT

Results and Discussion Soil sample results obtained in May and October 1986 were compared to evaluate:

1) Gypsum performance with and without ripping.
2) SSS performance with and without ripping.
3) Ripping performance versus flushing performance.
4) Straw performance versus manure.
5) Ripping with flushing performance.

The 1986 results are given in Table 6. Comparing this table to the results in Table 3 shows that ripping substantially improves the salt removal performance of gypsum. Because gypsum has a low solubility its penetration rate through undisturbed soil is slow. By ripping the soil, gypsum can be distributed more efficiently throughout the soil so that solubility is less of a problem. By comparison ripping did not improve the salt removal performance of SSS. Since SSS is a liquid it tends to collect at the bottom of the ripped layer. This prevents an adequate calcium supply from reaching the soil that lies above.

Comparing the data for zones G and H in Table 3 with that of zones A and B in Table 6 indicates that flushing improves salt removal performance more than ripping does for both SSS and gypsum.

Comparing the soil sodium concentrations, that are given in Table 7, of zone A to those of zone C it can be determined that manure is a slightly more effective organic amendment than straw. During the dry fall, sodium left the 40-60cm layer of zone C while it accumulated in the 0-20 cm and 20-40 cm layers. The movement of salt from the lower soil layers to the upper layers is indicative of evaporation of surface moisture transporting dissolved salt upwards. During the same period the manure treated zone A continued to lose salt from the shallowest depth. Therefore a downward movement of salt was maintained in zone A during the same period. It was observed that manure formed a better surface seal that reduces moisture evaporation than straw did.

Comparing the results in Table 8 to those in Table 4 indicates that ripping and flushing a gypsum amended soil gives the highest sodium removal rates observed in 1987.

ZONE	SOIL DEPTH IN CM	Na %	EC %	SAR %
A	0-20	-61.8	-46.0	-52.6
	20-40	-43.2	-39.1	-35.2
	40-60	-35.1	-32.4	-16.7
B	0-20	-47.4	-29.3	-41.7
	20-40	-15.0	-36.4	-13.9
	40-60	-28.7	-25.2	-9.9
C	0-20	-77.8	-68.6	-67.9
	20-40	-55.7	-51.0	-35.7
	40-60	-38.1	-33.2	-20.2

TABLE 6 THE 1986 RIPPING ASSESSMENT RESULTS FOR THE ZONES A, B AND C SHOWING PERCENT CHANGE IN KEY PARAMETERS

CONCLUSIONS

Soil salt concentrations in the control zone increased during the study period as a result of surface moisture evaporation and low rainfall.

The amendment program that exhibited the largest salt removal rate included gypsum, ammonium nitrate and manure applications with soil ripping and flushing during the summer. The calcium product Saline Soil Saver performed better than gypsum when neither one was aided by ripping or flushing.

Manure was considered a better organic amendment than straw because it afforded better protection against surface moisture evaporation.

SAMPLE TIME	SOIL DEPTH IN CM	Na CONCENTRATION IN meq/l	
		ZONE A	ZONE C
May 86	0-20	354.67	346.00
20-40	243.67	259.00	
40-60	197.33	199.33	
Oct 86	0-20	127.07	72.17
20-40	138.63	114.00	
40-60	129.00	124.60	
May 87	0-20	120.00	109.90
20-40	139.67	134.33	
40-60	135.33	112.33	
Sept 87	0-20	26.33	22.43
20-40	53.33	59.27	
40-60	59.40	75.03	

TABLE 7 CHANGE IN SOIL SODIUM CONCENTRATION
IN THE RIPPED ZONES A AND C

ZONE	SOIL DEPTH IN CM	Na %	EC %	SAR %
A (ripped/flushed/ manure)	0-20 20-40 40-60	-27.3 -35.5 -38.3	-25.9 -40.1 -40.5	-41.5 -44.7 -42.0
C (ripped/flushed/ straw)	0-20 20-40 40-60	-26.8 -29.0 -18.2	-28.6 -30.1 -20.5	-38.9 -30.4 -13.0

TABLE 8 RESULTS OF THE 1987 FLUSHING OF A RIPPED
SOIL SHOWING PERCENT CHANGE IN KEY PARAMETERS

RECOMMENDATIONS

The following is a recommended reclamation program for dispersed brine contaminated agricultural soils in a semi-arid climate based upon these findings and past practices.

1.) Determine the degree of contamination by conducting a soil sampling program. The results of this analysis should provide a soil calcium requirement as well as nutrient demands.
2.) Assess the drainage characteristics of the site, taking into account the soil texture. Install underground drainage such as weeping tile if needed.
3.) Apply calcium in the form of gypsum as specified by the soil analysis. Saline Soil Saver is not recommended because gypsum with ripping and flushing has been found to perform better.
4.) Apply fertilizers such as 34-0-0 to promote revegetation.
5. Thoroughly rip the soil to approximately 75cm to break up surface hard panning and to improve gypsum penetration.
6.) Liberally apply an organic amendment, preferably well aged manure (e.g. 10-15cm thick).
7.) Rototill the above treatments into soil at least 15cm.
8.) Provide some type of irrigation to maintain the downward leaching of excess salts. In areas that are distant from a water supply tanks may be rented and filled from water trucks or if the demand is high enough a portable irrigation unit might be purchased to serve a a number of sites at once. Irrigation rates need not be high therefore pumping demands can be minimized. A soaker hose design or drip style irrigation is sufficient.

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AKNOWLEDGEMENTS

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ADVANCING SPILL COUNTERMEASURE TECHNOLOGY WITH AQUEOUS FOAM

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Division Mine Safety Appliances Company

Chemical spills can occur wherever chemicals are manufactured, stored, packaged, transported and processed. Many of these spills involve only a few liters; however spills involving several thousand liters of material are not infrequent. A total of 8,116 spill or leak incidents from railcars alone was reported from 1976 to 1987 for the twenty states having the most incidents.[1]

Even though we implement the best current design technology for chemical handling and containment equipment and train operating and maintenance personnel to minimize the likelihood of spill occurrences, accidental spills of hazardous chemicals must be anticipated and steps planned to counter the consequences of spills. The consequences may be threats to personnel and facility security, toxic material threats to ground and water ecosystems and releases of airborne contaminants which can be cause for evacuation of downwind neighbors.

Effective response efforts are the result of planning and utilizing spill countermeasures which can reduce spill consequences. Some countermeasures used against chemical spills are:

- contain
- cover
- dilute
- neutralize
- collect

These countermeasures may suffice for low volatility chemicals which do not pose threats to neighboring areas. However, volatile or reactive material spills require countermeasures which can reduce fume releases from the spills.

One method of reducing fume releases from spills uses aqueous foam to cover or blanket the spill. This method has been demonstrated to be effective for hydrocarbon and polar organic liquids and some acidic and basic chemicals. Foam concentrates used against these materials include aqueous film forming foam, polar compound foam, protein foam and synthetic foam.[2] However, when applied to anhydrous chemicals like ammonia and sulfur trioxide or to water reactive chlorides such as titanium tetrachloride and chlorosilanes the fume suppression performance of these types of foams was questionable.

This paper describes some recent developments of an aqueous foam system designed to have improved capabilities for moderating fume releases from both contained and free spills of water reactive chemicals.

WATER REACTIVE CHEMICAL SPILL INTERACTIONS

When water reactive chemical leaks occur, a fume cloud comprised of acidic or basic vapors, aerosols and particulates forms, envelopes the area and is carried downwind. The fume cloud is created by vaporization of the spill chemical and its hydrolysis by atmospheric and spill substrate moisture. If the cloud is negatively buoyant, wind may not effectively disperse the toxic materials to reduce their concentrations to tolerable levels. Countermeasures used against these kinds of spills need to address not only the primary spill but also the materials which become airborne. Methods used for suppressing vaporization of spill materials include minimizing the spill surface area, reducing heat transfer into the spill and blanketing the spill with non-reactive covers which float on the spill.

For free spills with minimal depth, sorbents and neutralizers may be effective for reducing the spill vaporization rate and fume releases. With these kinds of measures, however, the need for proper waste management of the sorbent materials must be recognized.

When aqueous foam is applied onto a spill, the heats of solution and hydration will likely cause the spill vaporization rate and fume release to increase. This condition will be maintained until the spill is diluted and its vapor pressure reduced. Spill dilution occurs as water drains from the foam into the spill. If the water drainage rate into the spill can be inhibited, however, the foam cover can suppress fume release from the spill.

FOAM SYSTEM AND SPILL PARAMETERS

Aqueous foams are produced from water mixtures of foam concentrates containing surfactants and hydrophilic stabilizers. Foam properties such as expansion factors, liquid drainage rates and chemical compatibility are dependent upon the specific additive formulations used in the foam concentrates. If foam is to be successfully used for reducing the fume release from a chemical spill, its properties must be compatible with the spilled chemical and hydrolysis products. The foam expansion factor relates the foam volume to the liquid solution volume contained in the foam. Foam having a greater expansion factor contains less water than low expansion factor foam. The liquid drainage rate gives a measure of foam stability and its ability to retain water within its structure. Chemical compatibility of foam is a measure of its tolerance to pH excursions, permeability to vapors and particulates and life over a spill.

Purportedly, a "dry" foam, high expansion factor, cover is beneficial for moderating the hydrolysis of water reactive chemicals and therefore can reduce fume releases from spills. A "wet" foam, low expansion factor, cover usually causes increased vaporization and hydrolysis of the spill material and increases fume release. A slow liquid drainage rate foam also is helpful in reducing the rate of hydrolysis and fume release. However, the foam must also have chemical compatibility or the spill vapors may cause the foam to collapse before a cover forms. When this occurs, water contained in the foam can enter the spill rapidly and increase fume generation.

In addition to the spill material and foam characteristics, spill configuration can influence effective use of foam as a spill countermeasure. Tank farm spills may be directed by trenches to impoundments. Effectively covering these spills with foam may best be accomplished by fixed-installation equipment. Semi-fixed and mobile foam equipment may be the choice for covering free spills which occur at open area locations in plants or along transportation routes. Another concern for chemical compatibility arises from the fixed-installation system aspect. Foam must be producible with fume laden air without compromising foam quality or fume suppression capability.

FOAM DEVELOPMENTS

Recent efforts have been taken to develop a synthetic aqueous foam having improved water reactive chemical spill fume suppression capability. This work focused on those foam characteristics which would improve the fume suppression capability of aqueous foam. Titanium tetrachloride was chosen as the challenge spill chemical because it readily hydrolyzes to generate a dense fume cloud containing hydrogen chloride and particulates which limit visibility. These kinds of materials are commonly generated when water reactive chemicals leak or spill.

Initial foam/chemical compatibility evaluations were performed using approximately 0.5 liter of titanium tetrachloride contained in straight sided glass dishes and 1.0 liter contained in slope sided nickel pans. The titanium tetrachloride was covered with 0.9 to 1 meter of high expansion foam or 0.2 to 0.3 meter of medium expansion foam. Foams which demonstrated sufficient chemical compatibility to reduce fume releases in the laboratory scale tests were then tested against 20 liter spills contained in 0.6 sq. meter pans.

The foam which showed the most effective fume release capability was used on a 55-60 liter free outdoor spill of titanium tetrachloride. The titanium tetrachloride was spilled onto concrete and flowed freely to cover an area of about 35 sq. meters. The spill was then covered with foam and the fume suppression effectiveness observed. This foam was also tested against contained, 1.5 sq. meter, trichlorosilane spills and fires to demonstrate both its fume suppression and fire control capabilities.

RESULTS DISCUSSION

The liquid drainage rate and expansion factor play a discernible role in the fume suppression capability of aqueous foam. Figure 1 shows the liquid drainage characteristics for rapidly and slowly draining foams produced using the Type FR foam concentrate investigated during this work. The drainage characteristic of rapidly draining foam is shown by the "S" shaped curve for which the quarter drainage time is about five minutes; commercial fire fighting foams have similar characteristics. Slowly draining foam is characterized by the curve showing a quarter drainage time greater than twenty-five minutes. The rapidly draining foam was produced from a 2 percent concentration foam agent/-water mixture while the slowly draining foam was produced from a 6 percent mixture.

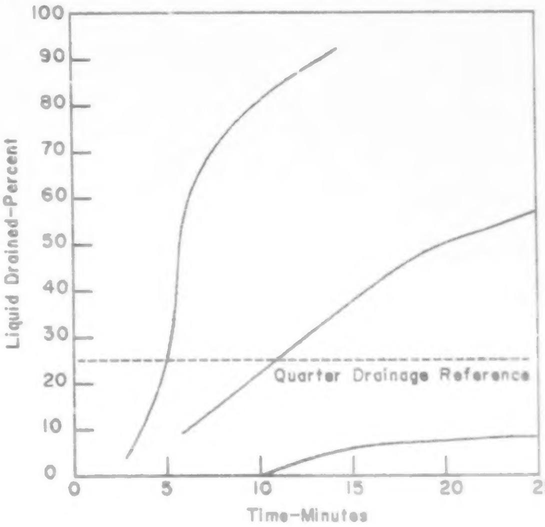

Figure 1 - Liquid Drainage Features of Fast and Slow Draining Foam

The effect of expansion factor on the drainage rate for a 6 percent mixture foam is shown in Figure 2. These data show that the drainage rate of lower expansion factor foam is greater than that of high expansion factor foam and that both the foam agent/water mixture concentration and expansion factor can influence the drainage characteristics. During the chemical compatibility phase of this work, the effect of expansion factor-drainage rate on fume suppression performance was observed. Fume release from titanium tetrachloride spills through 300:1 to 600:1 expansion factor foam was less than release through 50:1 to 150:1 foam.

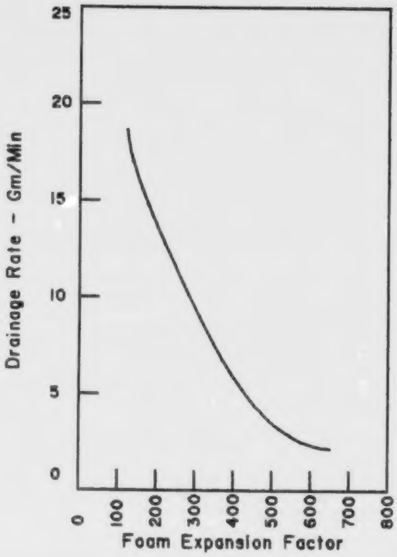

Figure 2 - Drainage Rate for Type FR Foam

After foam was applied, a gel agglomerate formed on the surface of the titanium tetrachloride. The gel consistency varied from a reactive rigid mass to a quiescent fluid floating on the spill. When high expansion factor foam was used, the gel was fluid and much less reactive than when medium expansion factor foam was applied. In addition to suppressing visible fumes released from titanium tetrachloride, the foam inhibited hydrochloric acid vapor release from the spill after the initial hydrolysis. Hydrochloric acid vapor concentrations over a one liter, 0.09 sq. meter, spill ranged from 160 to 330 ppm. After applying a one meter deep foam cover over the spill, the hydrochloric acid vapor concentration increased to 800 ppm. The concentration increase is caused by the initial hydrolysis of the titanium tetrachloride and is not an uncommon event. The acid vapor concentration then decreased to 10 ppm within fourteen minutes after initial foam application. The concentration was maintained at this level for twenty minutes after which the foam cover was removed. The gel agglomerate was then agitated and titanium tetrachloride exposed; the hydrochloric acid vapor concentration increased to 300 ppm verifying that reactive chemical still remained. Larger scale, 0.6 sq. meter, outdoor tests confirmed the small scale fume suppression results.

Fumes released from spilled titanium tetrachloride were injected into the air inlet of a high expansion foam generator positioned over the spill to determine the effect of contaminated air on foam producibility. Comparison of video recordings of foam generated using "clean" and fume-contaminated air showed that foam producibility was not degraded by the fumes.

Type FR high expansion factor foam was subsequently demonstrated on a free outdoor titanium tetrachloride spill and a contained 1.5 sq. meter trichlorosilane spill. These demonstrations were conducted in cooperation with a user and manufacturer of these chemicals. The foam easily covered and suppressed fume releases from the titanium tetrachloride spill within three minutes after foam production was started.

This foam was also shown to effectively suppress fume releases from trichlorosilane spills within two minutes after beginning foam application. When applied to ignited trichlorosilane Type FR foam was capable of suppressing fume release after four minutes and fire extinguishment within five minutes.

SUMMARY

Chemical spill countermeasure technologists utilize a variety of methods to alleviate spill consequences. Aqueous foam designed for use on water reaction chemical spills offers the technologist a means of suppressing fume releases from these kinds of materials.

One recently developed aqueous foam which has demonstrated improved fume suppression capabilities on titanium tetrachloride and trichlorosilane spills is Type FR. This foam is a synthetic type and has the following characteristics:

- Foam agent/water mixture; 6 percent
- Expansion factor; 300:1 to 600:1
- Drainage rate; less than 1.5 percent/min
- Gel forming
- Resistant to fume contamination.

These characteristics enable Type FR aqueous foam to cover acidic water reactive chemical spills while moderating hydrolysis and suppressing fume release. Its resistance to fume contamination also gives the spill countermeasure technologist flexibility in planning and designing not only remote manual responses but automatic fixed foam systems as well.

Aqueous foam can reduce the consequential impact of water reactive chemical spills. However, selecting the proper foams and integrating their capabilities into a countermeasure program are not elementary tasks. Many times isolating the spill and maintaining its quiescent state may be the preferred response; other spill events may require additional responses where proper aqueous foam application may be an effective countermeasure.

REFERENCES

[1] U.S. Department of Transportation.

[2] Evaluation/Development of Foams for Mitigation of Air Pollution From Hazardous Spills, U.S. EPA Report No. 600/2-82-029, June 1982.

VOLATILE LIQUIDS IN SEWERS: BEHAVIOUR AND COUNTERMEASURES

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1. Introduction

Volatile and flammable substances spilled into sewers can pose a serious explosion threat. In 1986 gasoline explosions in sewers and the subsequent fires caused a 13-block area in Saint John, New Brunswick, to be evacuated. Three buildings were destroyed in the subsequent fire. There were fortunately no serious injuries or deaths. The gasoline came from a leaking underground storage tank.[1,2] Despite the seriousness of such incidents, little work has been done on the countermeasures for volatile liquids in sewer systems. Countermeasures evaluated in this paper include the use of dispersants, foams and heavy gases.

Dispersants have been used for flushing spills into sewers and also for materials already in sewer systems. Proponents of this technique have claimed that this reduces the fire potential and offers a safe,convenient means of deal with spills of flammable or explosive products in an urban environment. [3,4] The hypothesis for such usage is that dispersants would put the majority of the material into the sewer water and thus lower the vapour concentration below the lower flammability limit and below the lower explosive limit. Dispersants for this countermeasure have never been quantitatively examined.

The use of foams in sewer spills has not been well documented. Foams work by forming stable bubbles (foam) over a vapour source so that the vapour cannot penetrate and thus is contained. Vapour suppression by foams has been tested and reviewed by a number of workers.[5-10]

The use of heavy gases to suppress fires or flammable vapours is quite well-established and is the principle behind many common fire extinguishers and also behind the use of halons in building fire-suppression systems. Evidence of the use of a heavy gas to specifically control flammable vapours in a sewer system, was not found in the literature.

The purpose of this study was to examine each of these countermeasures techniques using a model sewer system. The basic criterion used to evaluate the effect of the countermeasure is the amount of vapour in the sewer, both in terms of peak concentration and well as in terms of the total integral of vapour along the sewer.

Automotive gasoline and diesel fuels were used as the test fluids. It is believed that the results are applicable to spills of hexane, naphtha, benzene, toluene, xylenes and many other volatile hydrocarbons.

2. Experimental Techniques and Materials

A model sewer was constructed. The basic features of this system are illustrated schematically in Figure 1 and photographically in Figure 2. The sewer model consisted of a 104 m length of 3.8 cm diameter pipe, which descended at a constant slope of 0.0048 to a sump. Water was supplied from a constant head tank through valves, resulting in a constant flow rate throughout an experimental run. Fuel spills were introduced at a head box which contained a concrete pad, designed to resemble a street, sloping toward a drain just above the water of the sewer.

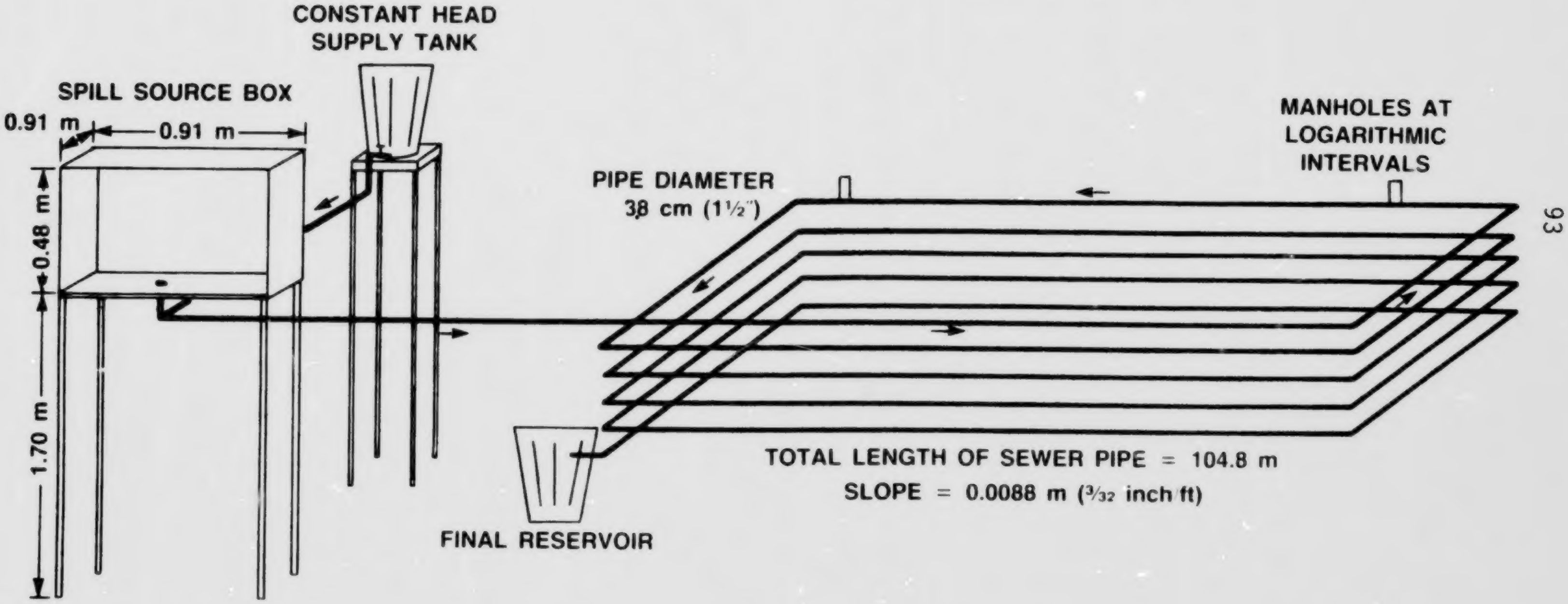
Simulated manholes or ports were placed along the sewer pipe at approximately logarithmic intervals (4.5,9.0,18.0 m, etc.) starting from the headbox. These served as access ports to sample vapours as well as providing vapour space to simulate real sewer manholes. Sample probes of HNU photoionizer model PI 101 vapour sensors were placed into the manholes at a distance of 10 cm from the sewer pipe. This distance was established to be one that yielded the best repeatability during a number of preliminary tests.

The HNU sensors were calibrated for measurement of both test fuels, non-leaded automotive gasoline and automotive diesel fuel, using Tedlar bags of known volume.[11] Volumes of fuel necessary to achieve the desired concentration were injected into air-filled bags, and an HNU probe attached to directly sample the mixture. At least two instruments were used during calibration runs to ensure that no instrument peculiarities existed. The data from the calibration runs were fitted to a quadratic equation, and this equation was used in a computer program during actual runs to provide output directly in parts-per-million (ppm) (by volume) of whichever fuel was being tested. Sensors, calibration software and computer were checked throughout the study by applying voltages to the computer inputs and comparing the results to manually-drawn calibration curves.

The outputs of the HNU instruments were directly coupled to Tecmar Labmate analog-to-digital converter which in turn was directly coupled to a Compaq 1 computer. A software program was prepared to operate the entire system and provide a real data output. On initiation of each run, sensor voltages were read 100 times to provide an average background voltage. This voltage was subtracted from subsequent readings to annul background signals. In practice, it was found that the backgrounds were very low and could have been ignored. The corrected voltage was used in the quadratic equation noted earlier to calculate ppm vapour. Data were presented on a real time display and recorded on a floppy disk. Floppy disk data were later printed on a second computer and analyzed. The computer program was designed to print out peak concentrations and also sum these concentrations with time to give an integral of vapour appearing at each sensor. These values are summed over all six sensors and presented in this paper as 'total integrals' and represent a measure of the total vapour in the model sewer system.

Three methods of fuel introduction to the sewer were used. Most experiments involved direct injections by syringe of 1 mL of gasoline or diesel fuel and countermeasure products were

Figure 1 **SCHEMATIC OF THE MODEL SEWER**


CONSTANT HEAD
SUPPLY TANK
SPILL SOURCE BOX
0.91 m
0.91 m
0.48 m
1.70 m
PIPE DIAMETER
3.8 cm (1½″)
MANHOLES AT
LOGARITHMIC
INTERVALS
FINAL RESERVOIR

TOTAL LENGTH OF SEWER PIPE = 104.8 m

SLOPE = 0.0088 m (3/32 inch/ft)

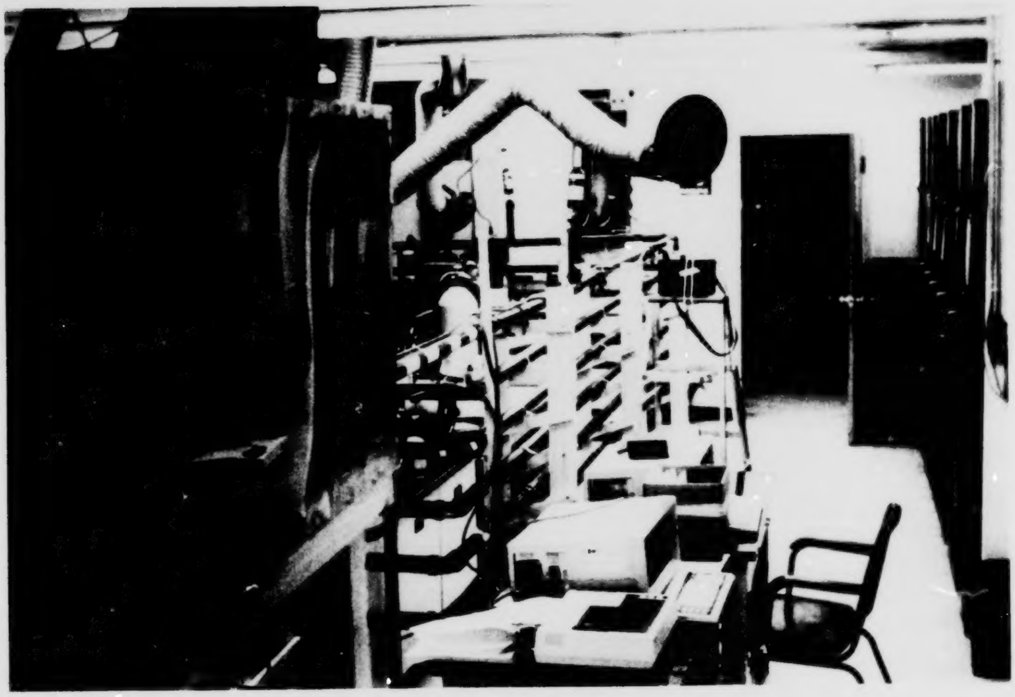


Figure 2 Photograph of The Model Sewer

similarly injected at various time intervals after the fuel introduction. In the case of dispersants, a 5% solution of the dispersant in water was injected 10 seconds after the fuel. This time was varied in early experiments to determine the effect on the results, and 10 seconds was determined to cause the least variability. The direct injection method simulates treating fuel spills already in the sewer. The direct injection of fuel in this manner was found to reproduce results from other introduction methods and also yield particularly consistent and repeatable results.

The second method of fuel addition was by mixing the fuel and treatment solution in a syringe and directly injecting into the sewer. This was performed to measure the effect of treatments when maximum contact and high mixing energy was available. This method was restricted to evaluating dispersant countermeasures.

The third method consisted of spilling fuel on a defined area of the concrete in the headbox and then placing the treatment solution on a defined (marked) area up-gradient from the fuel. This represents a situation where a fuel is flushed down the sewer with water, dispersants or foams.

During preliminary runs many fuel introduction techniques were tried, these made no difference to the final outcome or yielded significant data variance and thus were abandoned. Similarly, number of alterations were made to the model sewer system itself; placement of the vapour sensors, flow rates, temperatures and means of sampling water. Data reported here are derived from a final configuration of the system and significant variances are only reported. Over 150 runs were performed and recorded. This does not include trial runs during construction and testing, nor does it include spoiled runs after the configuration was finalized. The basic operating conditions are presented in Table 1.

Test materials were obtained from commercial sources as listed in Table 2.

As noted earlier dispersants were applied as 5% solutions in tap water. Foams were applied at the same concentration, however were mixed thoroughly before injecting with a syringe. Gases were admitted from a cylinder through a pressure regulator and a hose to the drain in the head box. Quantities were measured by timing the release and using this to calculate the mass flow from the pressure and mass flow measurements made at a later date. Data on exact pressures of release were lost and measurements are only known within an error of 150%. The regulators used were Matheson as was the mass flow meter. Solid products, dry ice and sodium bicarbonate, were also admitted with syringes with large openings.

Gas chromatographic (GC) analyses were performed using a Hewlett-Packard Model 5830A with a 3% SP-2100 (6-foot, 1/8") column operated with a temperature ramp of 8°C/min beginning at 40°C and ending at 220°C. Samples were withdrawn from manhole number 5 using a gas-tight syringe and directly injected into the GC. The timing of sample withdrawal was based on the known arrival time of the HNU-detected peaks, the arrival of which were very repeatable under the same operating conditions.

TABLE 1 Test Products

product	description	source
gasoline	non-leaded regular gasoline	PetroCan gas station
diesel	automotive diesel fuel	PetroCan gas station
Biosolve	dispersant sold for land and water fuel spills	Metra Chem Corp. Shewsbury, Mass.
Corexit 9527	dispersant sold for oil spills on water	Exxon Chemical Houston, Texas
Icoshine	dispersant sold for land spills	Illinois Chemical Chicago, Illinois
Jansolve	dispersant sold for land spills	Sunshine Chemical West Hartford,Conn.
Lestoil	household cleaning liquid	grocery store
Sunlight	household cleaning liquid	grocery store
Flame-out	vapour suppressing foam	Aaron Fasteners Ottawa, Ontario
AerO-foam	vapour suppressing foam	National Foam Lionville, Penn.
carbon dioxide	standard gas	Matheson Gas Ottawa, Ont.
Dry ice	food grade dry ice	made from gas above
Halon 1301	bromotrifluoromethane	Wormwald fire Sys. Ottawa, Ont.
Sodium Bicarbonate	regular lab grade	Fisher Scientific Ottawa, Ontario

TABLE 2 SEWER OPERATING CONDITIONS

SAMPLE POINTS

Number	Distance from Head-box (m)
1	0
2	4.5
3	9.0
4	18.0
5	51.4
6	104.0

WATER FLOW RATES

Flow Volume (L/min)	Flow Rate (m/s)	Retention Time (min)
1	0.18	10.0
2	0.22	7.5
3	0.24	7.1
5	0.29	6.0
10	0.34	5.1

WATER TEMPERATURE

12°C ±1°C

Water flow volumes were measured with a calibrated cylinder and stopwatch. Flow volumes were verified before each experimental run. Flow rates were measured by determining the retention time of a fluoroscein dye.

Water was sampled at taps from locations beneath vapour sampling ports numbers 3 and 5. Analyses were performed using a Horiba Oil-in-water meter Model OCMA-220; however concentrations in the water were too low to be detected (less than approximately 5 mg/L).

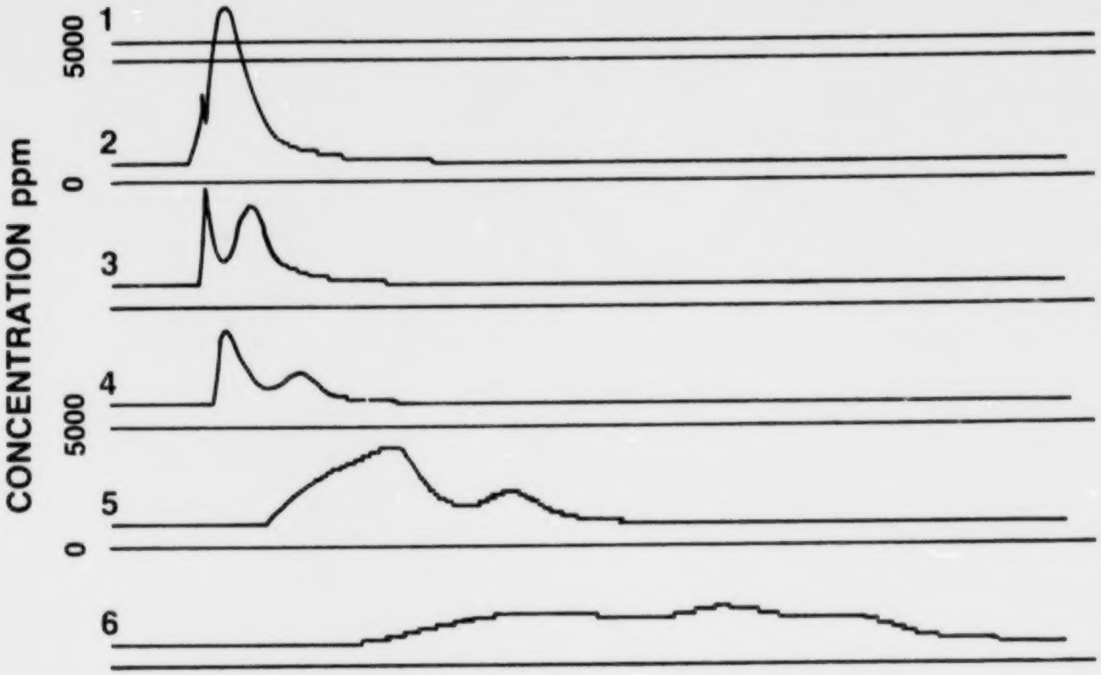
3.0 BEHAVIOUR OF FUELS IN SEWERS

A significant phenomena observed at the start of the study was that gasoline spilled into the model sewer produced two vapour peaks at sampling ports in the sewer system, whereas diesel produced only one. Figure 3 illustrates the two-peak phenomena for a test run involving gasoline alone and for one where dispersant was used on the fuel. This figure is a reconstruction of a computer real time display. Each display presents the vapour concentrations at each port (manhole). The X-axis is the time scale and each horizontal bar represents the vertical scale of 5000 ppm. Sensor 1, in the head box, does not detect any vapours as the fuel is injected, and the small amount that subsequently escapes is not detected in the large volume of air in the head box. The diagrams show that a sharp peak appears and is followed shortly thereafter by a broader peak. Both peaks flatten out significantly by the time they reach the last sensor (number 6) located 104 m from the head box. The two peaks move at different rates, the second one being slower than the first.

Samples were withdrawn of the air and were analyzed by GC as described above. The results are shown diagrammatically in Figure 4. It was found that the first vapour peak is formed from gasoline evaporating as it rides on the underlying body of sewer water. This peak moves at approximately the same speed as the sewer water and consists of the higher boiling fractions of the fuel. The second peak originates from fuel evaporating near the entry point and consists of the low boiling point fractions of the fuel. This vapour peak moves slowly through the sewer system, as its only driving force is the weak friction with the underlying sewer water. As can be seen from the gas chromatographic traces in Figure 4, compounds smaller than toluene are largely removed from vapour peak 1 when dispersants are used.

Diesel fuel injection resulted in significantly less vapour concentration in the system. The significantly lesser amounts of volatile components in the diesel fuel account for this. Gas chromatography analysis of vapour peaks show only minor fractionation between the leading and trailing edges of the vapour peaks.

CONCENTRATION AT EACH MANHOLE - gasoline only



CONCENTRATION AT EACH MANHOLE - dispersant flushed

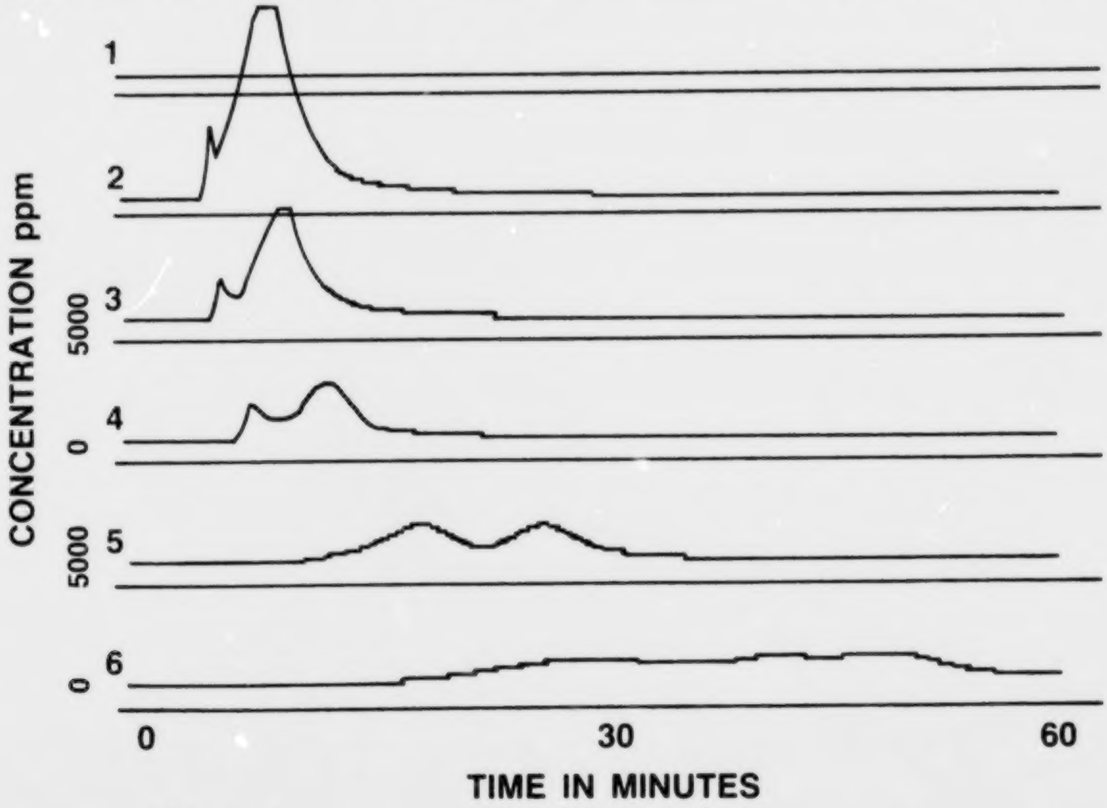
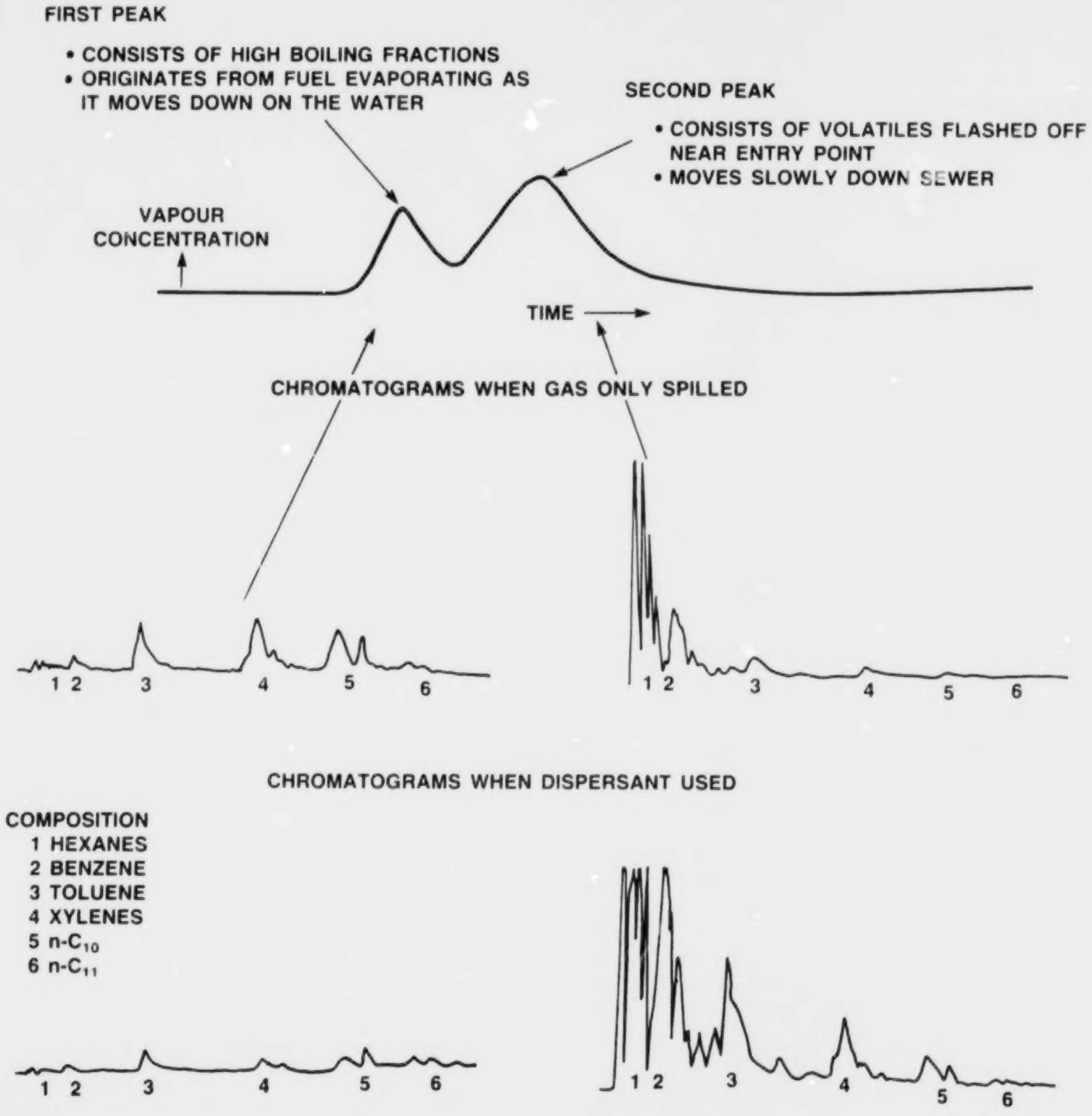


Figure 3

Figure 4

ORIGIN AND COMPOSITION OF VAPOUR PEAKS IN A SEWER



FIRST PEAK

- CONSISTS OF HIGH BOILING FRACTIONS
- ORIGINATES FROM FUEL EVAPORATING AS IT MOVES DOWN ON THE WATER

SECOND PEAK

- CONSISTS OF VOLATILES FLASHED OFF NEAR ENTRY POINT
- MOVES SLOWLY DOWN SEWER

CHROMATOGRAMS WHEN GAS ONLY SPILLED

CHROMATOGRAMS WHEN DISPERSANT USED

COMPOSITION
1 HEXANES
2 BENZENE
3 TOLUENE
4 XYLENES
5 n-C_{10}
6 n-C_{11}

In a previous paper, we have shown that as the amount of vapour increases in the sewer system, the velocity of its movement decreases.[12] This is an important finding in terms of spill countermeasures, any action which increases vapour content in a sewer also increases exposure to vapours and subsequently explosion potential both in terms of increased vapour to explode but also increases exposure time.

4.0 Use of Dispersants for Spill Countermeasures

In a previous paper, the present authors describe extensive experimentation on the use of dispersants in sewer systems.[12] The effect of dispersants on fuels already in a sewer system is to increase the volatilization rate of the fuel and thus increase the amount of vapours in every case. This is caused by the action of dispersants on the size of fuel droplets in the water. If dispersant is present and works, it produces fine droplets of the fuel in the water and this in turn increases the volatilization rate of the smaller fuel components. Dispersants have little actual dispersing effect on the smaller components of fuels such as hexane, benzene, etc. This has been noted by other authors as well.[13,14]

The results of the dispersant treatment on fuels in a sewer system is shown in Figures 5 and 6 for gasoline and diesel fuel respectively. These figures show that the peak concentration noted at the manholes is increased in every case through the use of dispersants. Figures 7 and 8 show the effect on the total amount of vapour in the sewers, here represented by the sum of the integrals of vapour appearing at each manhole. The total vapour content in the sewer system is plotted against the dilution volume which is the amount of dispersant solution used with respect to the volume of fuel spilled. Dispersant treatment also increases the amount of vapour appearing in the sewer. The flushing of additional volumes of dispersant solution has little beneficial effect. An additional effect that is observed in these figures is that there is little differentiation between dispersant products. They cause about the same level of vapour increase.

The effect of adding increased energy to the dispersant was also investigated in the previous study.[12] The increased energy increased both the peaks and the total amount of vapour in the sewer system. This is not surprising as the increased energy would make smaller and greater numbers of fuel droplets and thus increase the volatilization from these droplets.

5.0 Use of Foams and Heavy Gases on Fuels In Sewers

The effect of a variety of countermeasures on fuels already in the sewers was investigated. Two vapour-suppressing foams, Flame-out™ and AerO-foam™, were added as 5% solutions which had been shaken to form stable foams and these foams were injected 10 seconds behind the fuel injection, just as performed with the dispersants. Gases, Halon 1301 or bromotrifluormethane and carbon dioxide were admitted through a pressure regulator and subsequently through a plastic tube to be released at the same point as other treatments. Gas releases were timed to provide a

Figure 5

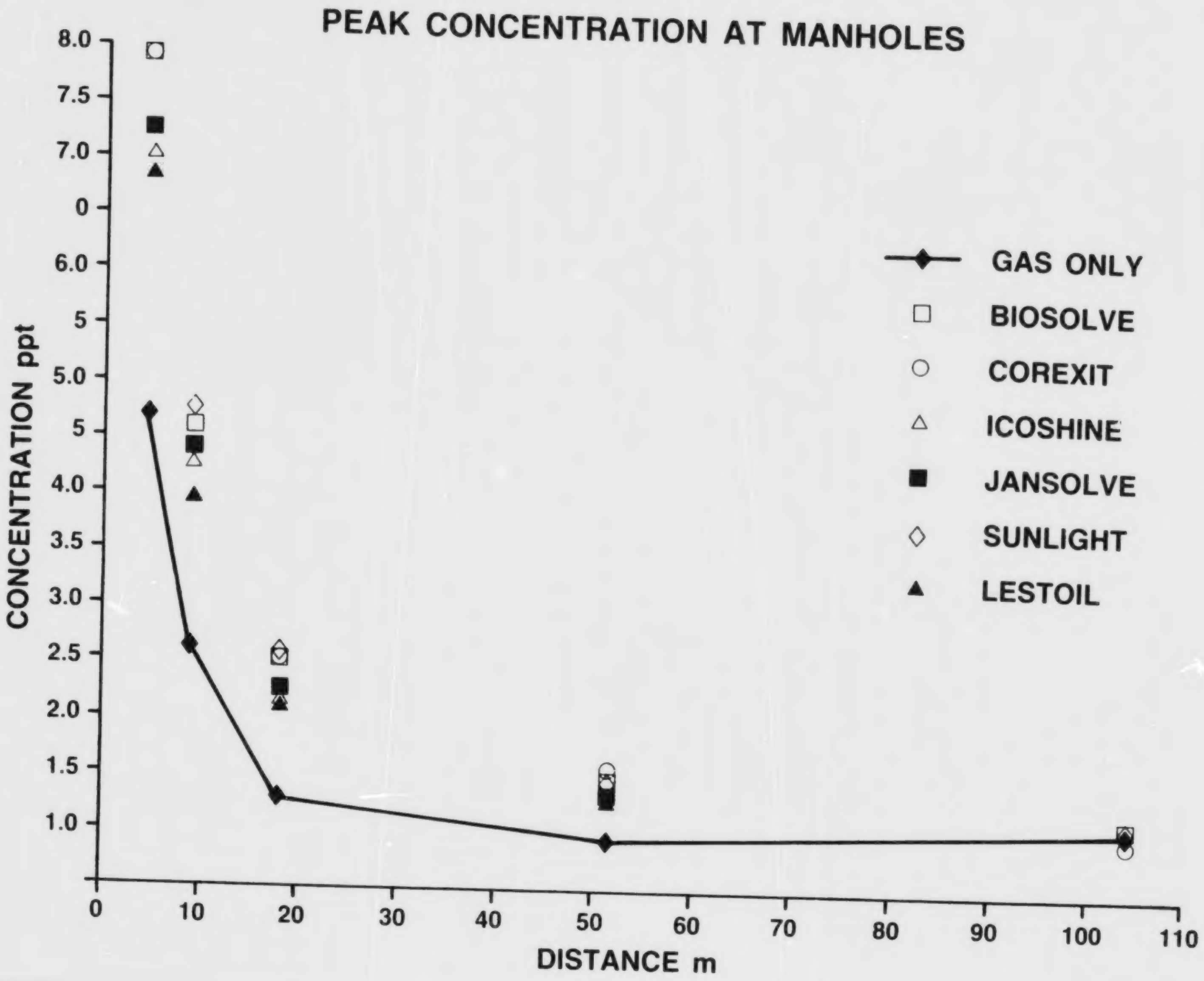

PEAK CONCENTRATION AT MANHOLES
CONCENTRATION ppt
8.0
7.5
7.0
0
6.0
5
5.0
5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
10
20
30
40
50
60
70
80
90
100
110
DISTANCE m
GAS ONLY
BIOSOLVE
COREXIT
ICOSHINE
JANSOLVE
SUNLIGHT
LESTOIL

Figure 6 TOTAL VAPOUR RELEASED INTO SEWER

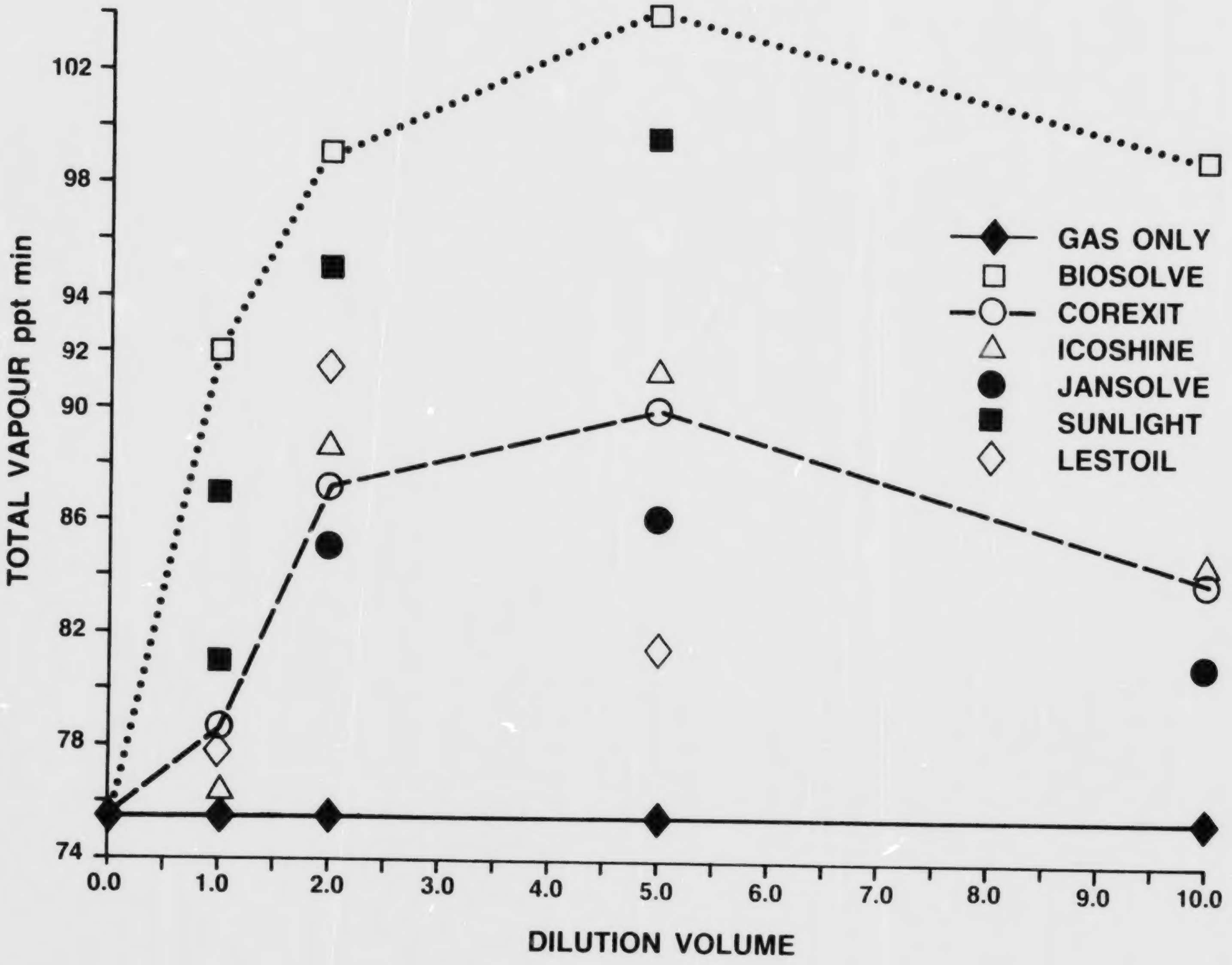


Figure 7

PEAK DIESEL CONCENTRATION AT MANHOLES

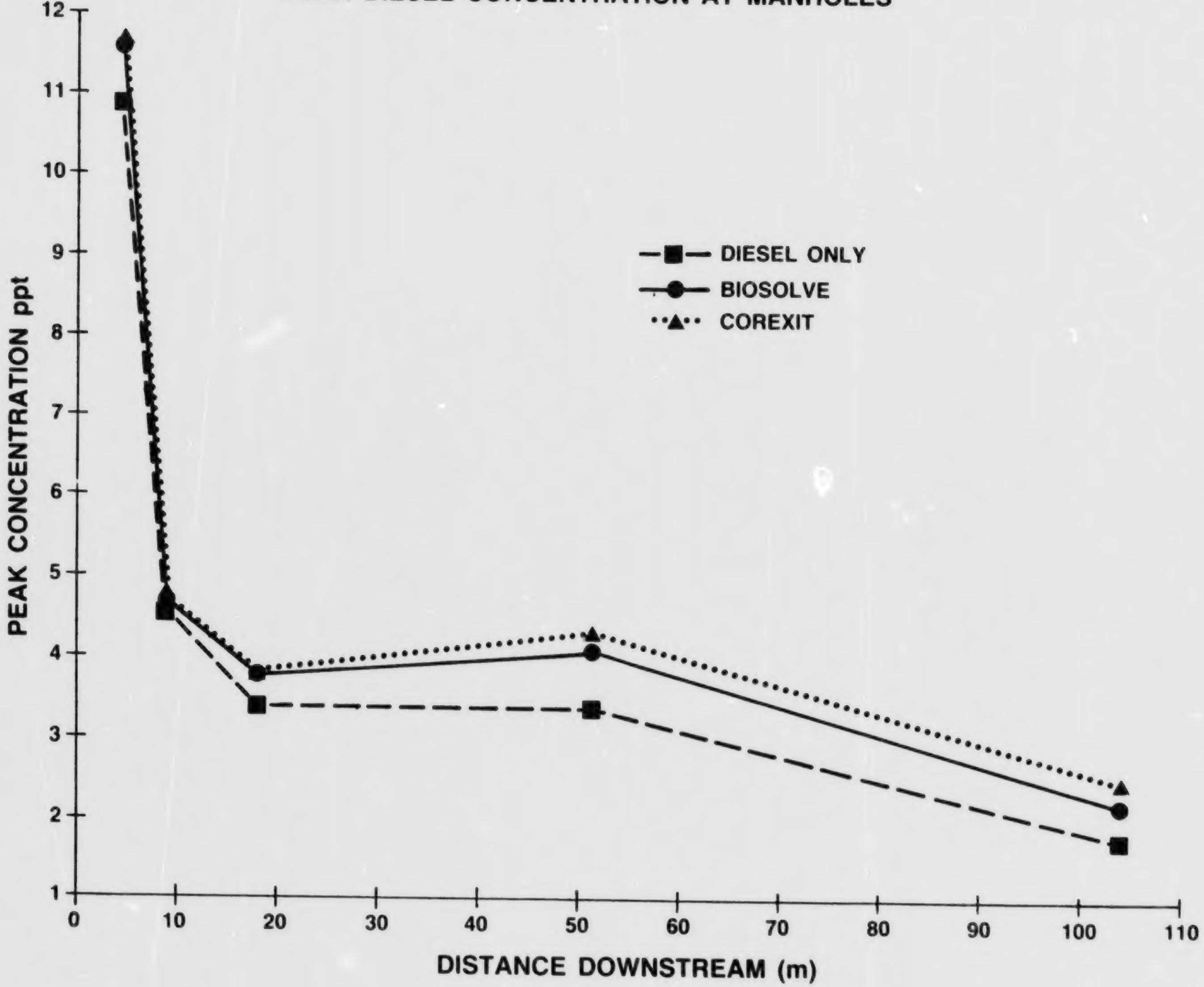
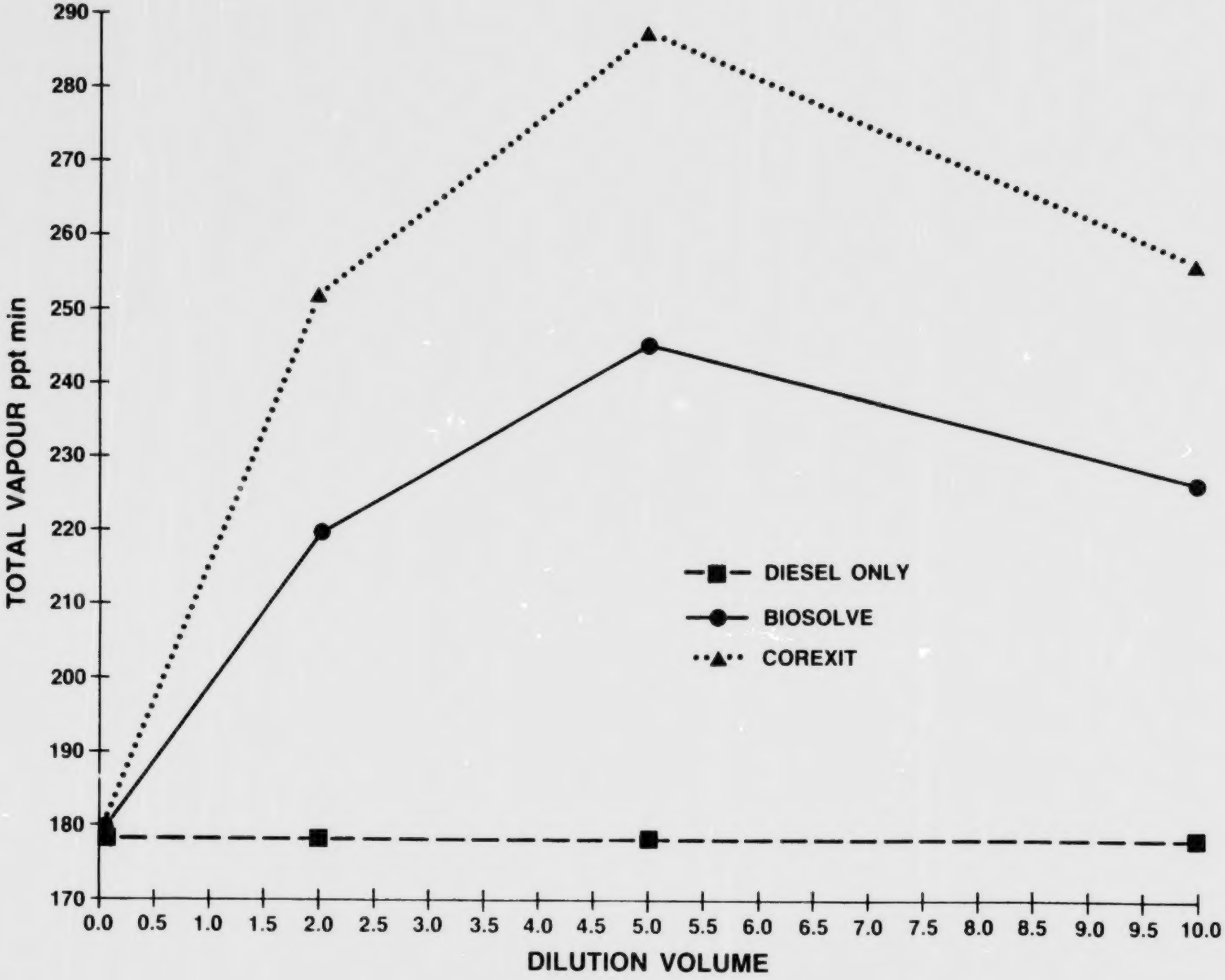


Figure 8

TOTAL DIESEL VAPOUR IN SEWER



measurement of volume. Solid products, sodium bicarbonate and dry ice were admitted using a large syringe and were again admitted at the same point in the drain. The foams were admitted in the same quantity as dispersants, generally 1 ml of a 5% solution, unless otherwise specified. Ten grams each of the sodium bicarbonate and dry ice were employed.

The effect of these countermeasures on peak concentrations of gasoline vapour at the various ports is illustrated in Figure 9. For illustrative purposes, the results from various countermeasures techniques are averaged. The effect of the foams on fuels already in the sewer is the same as that of dispersants, it increases the amount of vapour. It is suspected that this is due to the fact that most of the vapour is released before the foam can block further release, and also that the foams' surfactants have a certain amount of dispersing effect. To verify that foams have the ability to slow evaporation, a series of separate experiments were done with the two foams used in this study. It was found that both foams would suppress the evaporation of gasoline and diesel fuel in static situations.

Figure 9 shows that the two heavy gases carbon dioxide and halon are quite useful in reducing the peak concentration at the various manholes. It should be borne in mind when examining Figure 9, that more Halon was admitted than carbon dioxide. Illustrations of this are presented below.

Figure 10 shows the effect of these countermeasures on the total vapour or sum of the integrals at the six sampling ports. These results as well as those in the previous figure are derived from experiments with gasoline as a test medium. Again, it is demonstrated that foams and dispersants increase the total vapour in the sewer and that carbon dioxide and halon are very effective in reducing the vapour. The mechanism by which these heavy gases remove vapours is thought to be gravity displacement. This is illustrated in Figure 11 where it is shown that halon is more efficient than carbon dioxide in lowering the total vapour concentration. Halon has vapour density of 5.4 compared to that of carbon dioxide which is 1.5.[15] These are based on air having a vapour density of 1.0 at 20°C, approximately the same temperature used in this study. Figure 11 shows that halon is the most efficient, carbon dioxide admitted as a gas is the second most effective. Other forms of carbon dioxide admission, eg. as sodium bicarbonate and as a solid, dry ice, are not as effective.

The model sewer system contains an approximate air volume of 450 L. The amount of gas put in varied from 3 to 12 litres for the carbon dioxide and from 10 to 30 L for the halon. If these countermeasures were to be applied in the real world, small amounts could also produce significant effect. For example a carbon dioxide fire extinguisher often contains 5000 L at standard pressure and temperature, this would be sufficient at a similar ratio to that noted above (for example 10 L to 450 L, or 1:45) to treat a sewer pipe of 24 inches diameter (76 cm) for a length of 130 m.

EFFECT OF COUNTERMEASURES ON PEAK VAPOUR CONCENTRATIONS

Figure 9

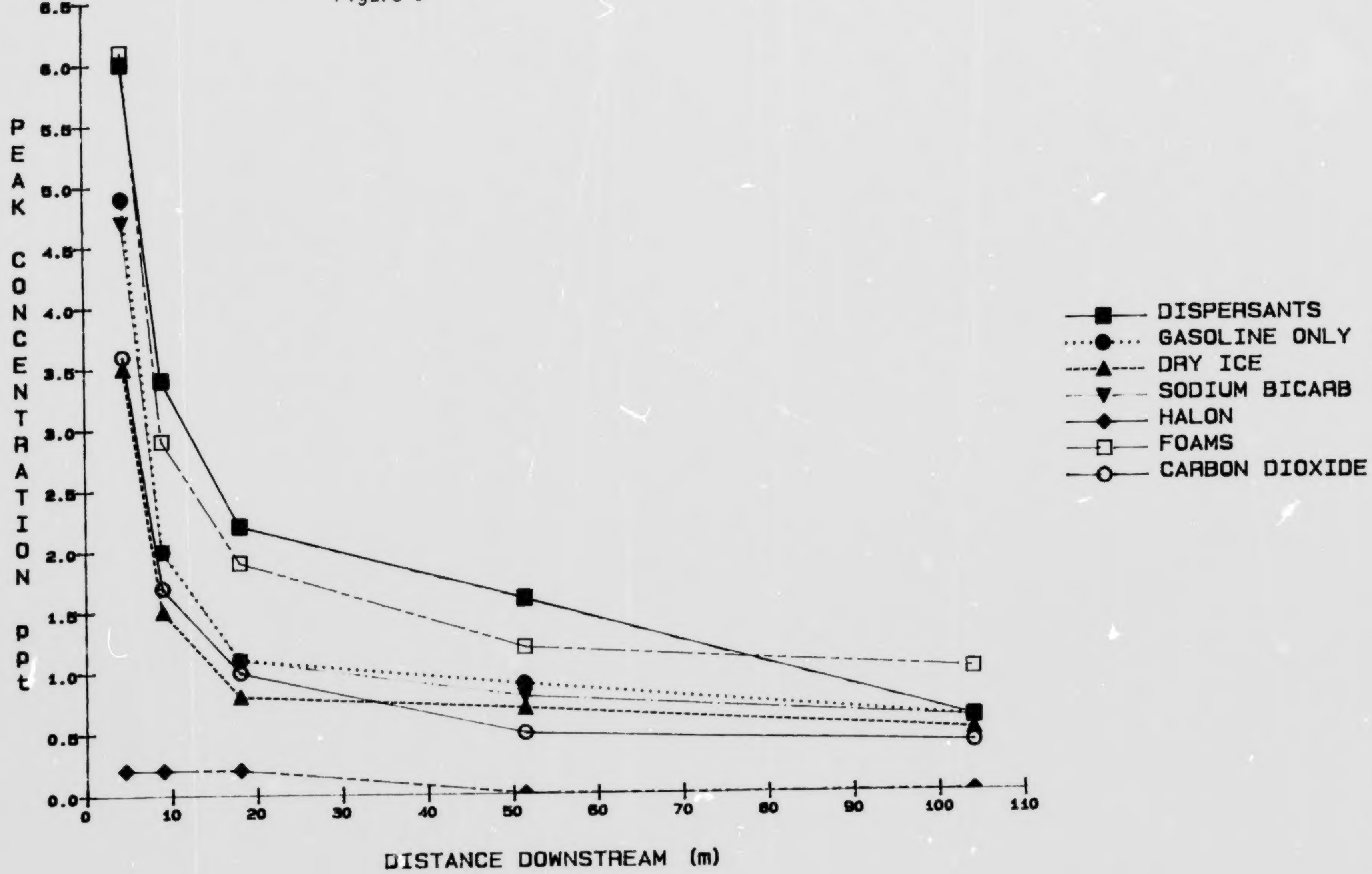
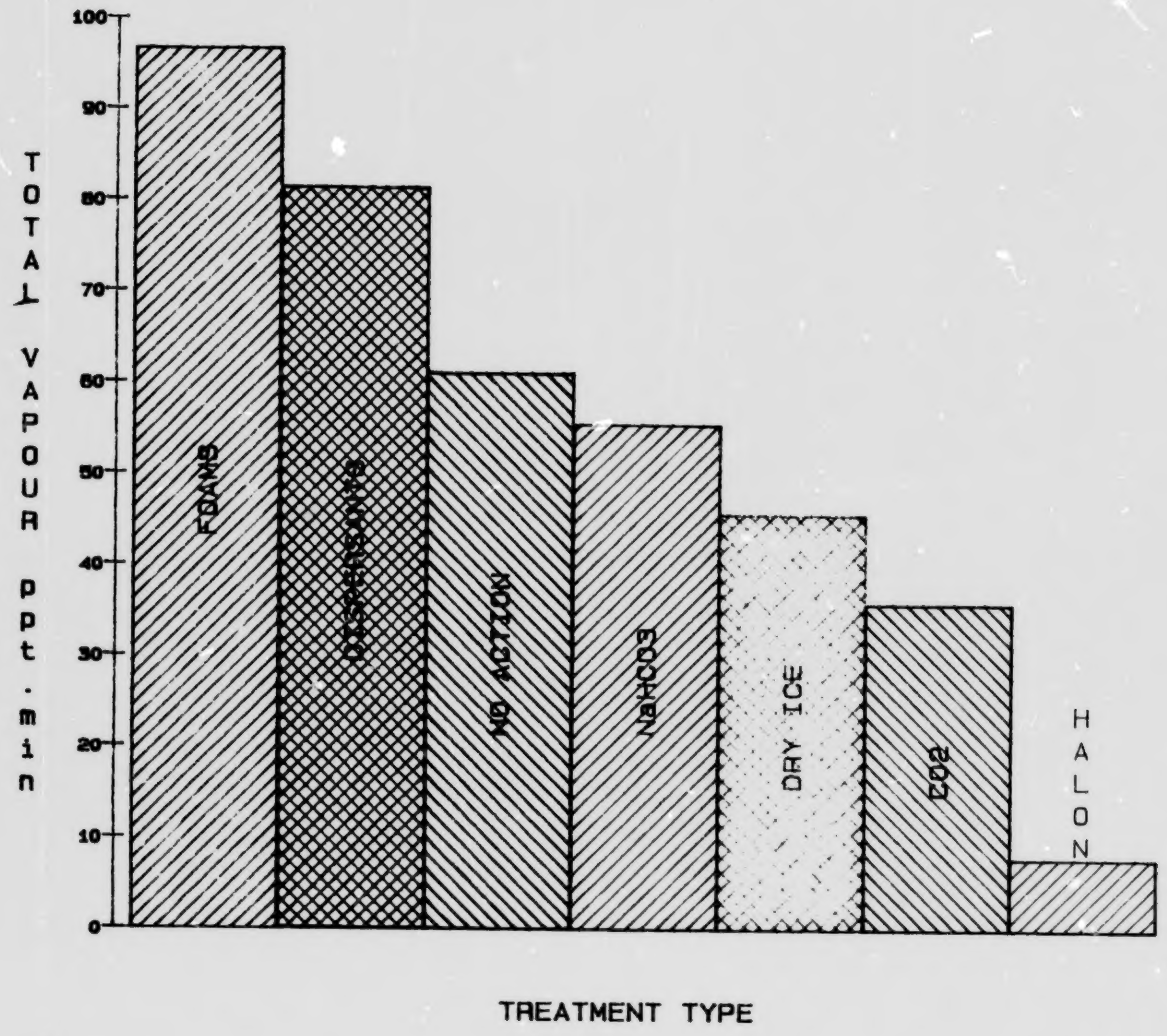
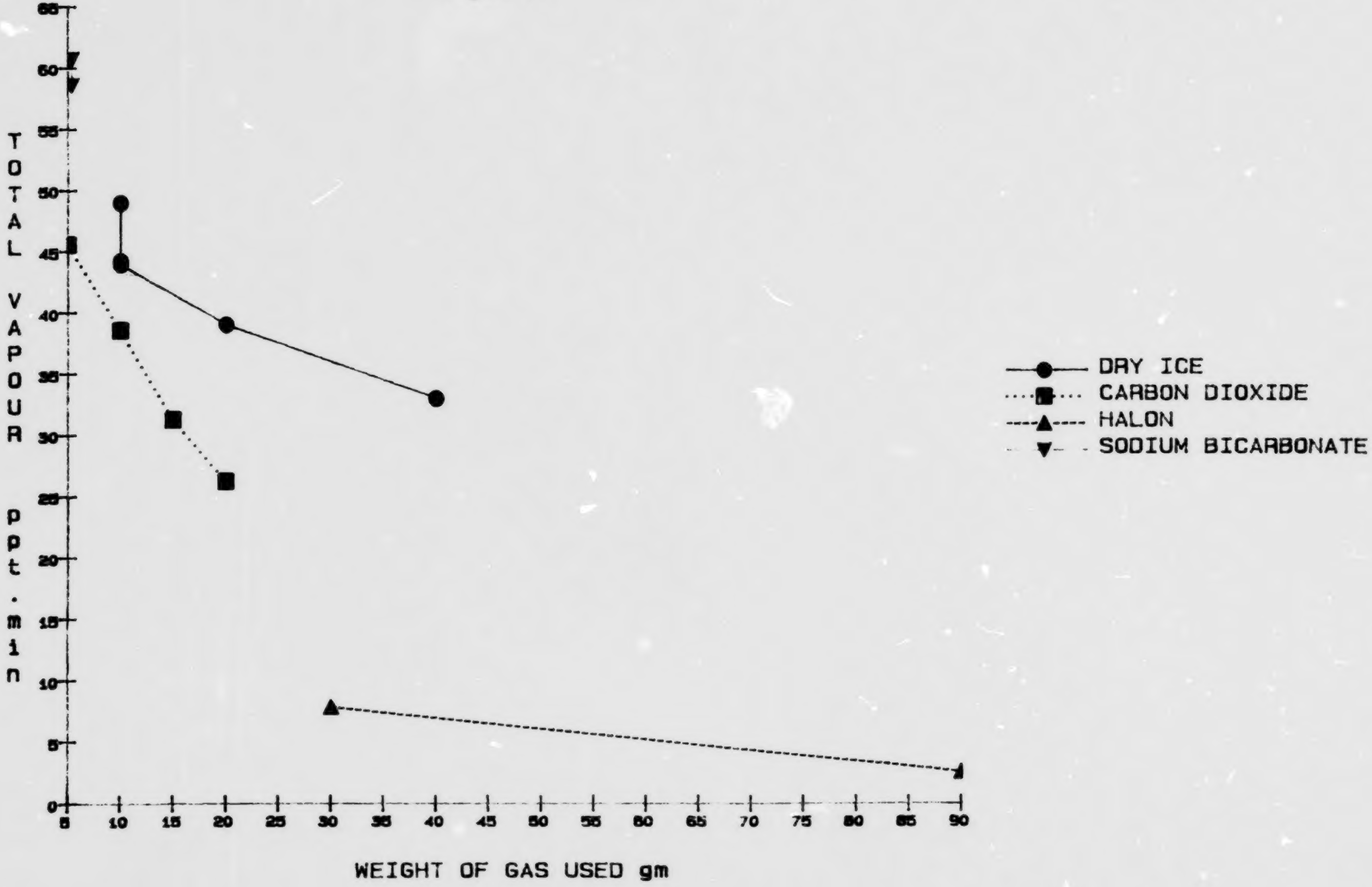


FIGURE 10 TOTAL VAPOUR IN SEWER AFTER TREATMENT



EFFECTIVENESS OF HEAVY GAS COUNTERMEASURES

Figure 11



6.0 Summary and Conclusions

Fuels and light hydrocarbons will evaporate to some extent when spilled into sewers. Lighter components will evaporate near the entry point and the resulting vapours will move slowly down the sewer system. Gasoline contains sufficient volatile components to produce two vapour peaks in the sewer system. The first is a more rapidly-moving peak which results from evaporation of fuel riding on the sewer water. The second peak is formed by the slower-moving volatiles resulting from evaporation near the entry point.

Dispersants used on fuel spills in sewers increases the peak concentrations of the vapour in the sewer as well as the total amount of vapour. Because of the increased vapour, the movement along the sewer is slower than when dispersants were not used. The use of vapour-suppressing foams on fuel spills in sewers yield the same results as for dispersants. The use of dispersants and foams on fuel spills in sewers is not recommended and if used, would result in greater potential for explosions as well as increasing the magnitude of an explosion compared to situations where dispersants are not used.

The use of heavy gases such as carbon dioxide or Halon 1301 reduces the peak concentration and total amount of vapour released into the sewer system. Halon is more effective, probably because of its greater density and specific gravity, but because of its expense and concern over its long-term fate in the environment, is not the wisest choice for spill countermeasures. Carbon dioxide is effective and offers a very practical countermeasure as it is widely available in fire extinquishers.

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A REVIEW OF COUNTERMEASURES FOR THE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER

by

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INTRODUCTION

On February 15, 1986 a Canadian National Railways freight train partially derailed near Fort Langely, British Columbia, Canada. Among the cars were several carrying 1,2-dichloroethane, commonly known as ethylene dichloride. Five of these cars left the track and 336,000 litres of ethylene dichloride were spilled.

The location of the spill was on the back of the Fraser River in what was once the river bed. The soil was sandy with very few clay lenses. As a result, the ethylene dichloride very rapidly penetrated the soil and disappeared. It then formed a column of contamination proceeding rapidly toward the water table. Some was stopped by the clay lenses but very little. Once in the groundwater, the ethylene dichloride began to dissolve and spread.

Remediation, which began shortly thereafter, consisted of pumping the contaminated water to the surface for treatment. By this time the water being pumped from the centre of the plume was 1 to 2 percent ethylene dichloride while several hundred metres away the concentration was 100 to 1,000 ppm.

The above example is typical of a spill resulting in volatile organic compound (VOC) contamination of groundwater. A further source of groundwater contamination is leaking chemical landfills.

The Gloucester Landfill, which is located near Ottawa, Ontario, was used by federal government laboratories to dispose of hazardous wastes (mainly organic solvents) from 1969 to 1980. Disposal was normally accomplished by burning or detonating the solvents in a pit or trench but, it was reported in 1972 that certain unnamed individuals had engaged in indiscriminate dumping. It is estimated that 160,000 litres of solvent were disposed of at the landfill.

In 1981, contaminants including diethyl ether, acetone and some chlorinated solvents were detected in the groundwater migrating from that portion of the landfill where the disposal had occurred. Subsequent studies revealed that the contaminants listed in Table 1 were present in the groundwater. Concentrations vary from low ppb's to 10's of ppm's. (Jackson, et al., 1985)

TABLE 1. ORGANIC CONTAMINANTS - GLOUCESTER LANDFILL

Methanol
Dichloromethane
Acetone
1,1-Dichloroethene
1,1-Dichloroethane
Tetrahydrofuran
Diethyl ether
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
1,4-Dioxane
Trichlorethene
Benzene
Hexane
Toluene
Chlorobenzene
2-Chlorophenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
2,3,4,5-Tetrachlorophenol
Pentachlorophenol

Leaking landfills which contaminate groundwater with VOC's may impact surface water shortly thereafter. This has happened in Sarnia, Ontario where each spring the rising groundwater table in a chemical landfill contaminates the water in the ditches along its border. Pollutants include ethylene dichloride, carbon tetrachloride, tetrachloroethene and several other chlorinated alkanes.

Several techniques for the removal of VOC's from groundwater have been investigated and/or used in cleanups. This paper will describe the various technologies and discuss their advantages and disadvantages. Emphasis will be on Canadian experience.

RESPONSE TECHNOLOGIES

General

The technologies known to have been investigated and/or used include:

a. Air stripping
b. Carbon adsorption
c. Biological treatment
d. Resin adsorption
e. Oxidation/reduction
f. Steam stripping
g. Reverse osmosis
h. Solvent extraction
i. Pervaporation

The first two technologies are widely used in the United States for the treatment of groundwater. Biological treatment has been used occasionally. The other technologies have been investigated at the laboratory and pilot plant scale. In Canada these studies have been carried out by Environment Canada's Wastewater Technology Centre (WTC), the Environmental Emergencies Technology Division (EETD) and several consulting companies. All have advantages which make them best suited for a particular situation but they all have disadvantages either when used in an application for which they are not suited or in terms of the products which they produce. (Whittaker, et al., 1987)

Air Stripping

In air stripping, as with all of the other technologies except in situ biodegradation, the groundwater must first be pumped to the surface for treatment.

As practiced for the removal of VOC's from groundwater, air stripping is normally carried out in a countercurrent packed column. Slowly falling films of water meet rising air to promote efficient phase transfer. The VOC's then exit the column with the air stream.

Henry's law and appropriate phase and interface (film) mass transport expressions that incorporate interphase concentration gradients can be coupled to describe, respectively, the thermodynamics and kinetics of the stripping process. Mathematical models are also available.

Air stripping is currently (December, 1987) being applied to the cleanup of the dilute portion of the EDC contaminated groundwater at Fort Langley, British Columbia and at a leaking chemical landfill at Ville Mercier, Québec. Several studies have also been carried out by consultants and WTC to determine the applicability of air stripping to situations such as the Gloucester Landfill (GLF). In one study, WTC investigated the effectiveness of air stripping for GLF leachate that had been pre-concentrated by reverse osmosis (RO). Air stripping was carried out using two 1.22 x 0.10 metre plexiglass columns packed with 1.27 cm Intalox saddles. Water flow rates of 0.5 and 2.0 litres per minute and air to water ratios of 30:1 and 150:1 were used. Analysis of the results, which are summarized in Table 2, showed that the air to water ratio was the most critical variable for optimum contaminant removal. (Simovic, et al., 1986)

TABLE 2. WTC 1984 AIR STRIPPING RESULTS

Compounds	Feed Concentration (ppb)	Range of Removal Efficiency (%)	Residual Concentrations (ppb)
Dichloromethane	9 - 1670	57 - 99	2.3 - 38.2
Acetone	750 - 36,000	32 - 99	67.4 - 9340.4
1,1-Dichloroethene	2 - 1531	43 - 99	0.5 - 130.2
1,1-Dichloroethane/THF	25 - 2671	25 - 99	6.4 - 667.9
Chloroform	800 - 40,100	31 - 99	33.6 - 2775.7
Diethyl Ether	136 - 2300	25 - 99	0.7 - 1294.0
1,2-Dichloroethane	22 - 653	24 - 99	1.6 - 228.6
1,1,1-Trichloroethane/ 1,4-Dioxane	12.6 - 40,685	2 - 99	12.5 - 813.7
Trichloroethene	2 - 280	41 - 99	0.5 - 63.4
Benzene	28 - 1350	25 - 99	1.2 - 78.2

The biggest advantage of air stripping is its cost (5¢ to 20¢ per 1,000 litres) but the result of the process may be the transfer of a water pollution problem to an air pollution one. As a result several jurisdictions, including the American states of California, New Jersey and Massachusetts, require the treatment of the exiting air. This can be done by oxidation, burning or adsorption. All increase the cost significantly.

In 1986, WTC investigated the use of granular activated carbon to collect the effluent gases from a pilot plant air stripping unit at the Gloucester Landfill. The water was pumped to the top of a 1.8 metre column, packed with Intalox saddles or Raschig rings, at a flow rate of 4 or 8 litres per minute. Air water ratio was varied from 20:1 to 110:1. The off gases were collected in two, series carbon columns, 50 cm in height by 25.4 cm in diameter, each containing 989 grams of Calgon 4X6 mesh BPL granular activated carbon. Analyses of the feed, air stripper effluent, air stripper off-gases and GAC off-gases were carried-out.

The best air stripping removals and the GAC carbon loadings are shown in tables 3 and 4. No contaminants were detected in the off-gases from the second carbon column. (Simovic, et al., 1987)

TABLE 3. WTC 1986 BEST REMOVAL EFFICIENCIES OBSERVED DURING AS TESTS

	4L/min;1.3cm RR; A:W = 110:1 Concentration (ug/L)			4L/min;1.3cm IS A:W = 70:1 Concentration (ug/L)		
Compounds	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
1,1-Dichloroethane	34	0.3	99.1	99	2.0	98.0
1,2-Dichloroethane	76	4.0	94.1	177	10.0	94.3
Chloroform	30	1.0	96.7	81	3.0	96.3
1,1-Dichloroethene	13	0.2	98.5	115	2.0	98.3
1,1,1-Trichloroethane	41	0.1	99.8	24	0.3	98.7
Benzene	11	0.1	99.1	107	0.4	99.6
Toluene	5	0.3	94.0	49	0.3	99.4
Trichloroethene	17	0.2	98.8	81	1.0	98.8

RR = Raschig Rings
IS = Intalox Saddles
A:W = Air to Water Ratio

TABLE 4. WTC 1986 GAC LOADINGS - ACTUAL AND PREDICTED

Compounds	Influent Conc. (ug/L) STP*	Actual (mg/gm C)	Predicted (mg/gm C)
1,1-Dichloroethane	3.5	71.50	-
1,2-Dichloroethane	6.2	32.86	36.69
Chloroform	3.5	30.15	-
Benzene	9.3	51.62	78.68

* Standard temperature (0°C) and pressure (1 atm)

Carbon Adsorption

Adsorption is a partitioning process in which a contaminant is transferred from a dissolved state in the aqueous phase to the surface of a solid phase. The process of adsorption onto activated carbon involves contacting the contaminated water with the carbon, usually by allowing it to flow through a series of packed bed reactors. The activated carbon selectively adsorbs organic constituents by a surface attraction phenomenon in which organic molecules are attracted to the internal pores in the carbon granules. It is an equilibrium phenomenon which is, at least at lower levels, strongly concentration dependent. Eventually the carbon becomes saturated and requires regeneration or disposal.

The primary advantage of activated carbon adsorption is its low cost, 50¢ to $3.00 per 1,000 litres. It is, however, simply a means of transferring the contaminant between phases. Increasingly jurisdictions are banning the landfilling of organically contaminated carbon. The US EPA has done so effective 1 January, 1988. Decontamination increases the costs substantially.

Canadian experience with activated carbon includes drinking water purification and industrial waste streams as well as the Ville Mercier and Sarnia landfills. Several studies have also been carried out by WTC, EETD and Canviro Consultants at the Gloucester Landfill. In the last named study the contaminated groundwater was treated with GAC, in a bench scale reactor, at 2,000 mg/litre. The results are shown in Table 5. (Canviro Consultants, et al., 1984).

TABLE 5. CANVIRO 1983 GLOUCESTER STUDY
(2,000 MG/L)

Chemical	Concentration(ppb)	% Removal
Dichloromethane	183	68.9
Acetone	799	75.7
1,1-Dichloroethene	2	100
1,1-Dichloroethane	65	84.6
Chloroform	1579	94.9
1,2-Dichloroethane	53	94.3
1,1,1-Trichloroethane	283	98.9
Trichloroethene	43	100
1,1,2,2-Tetrachloroethane	8	0
Diethyl Ether	105	94.3

The main conclusions from the GAC portion of the CANVIRO study were that:

a. GAC is a treatment process capable of reducing all of the contaminants to within their groundwater quality objective;
b. the use of air stripping prior to GAC would reduce the carbon usage by approximately one-third; and
c. acetone is not effectively removed by GAC.

Biological Treatment

In contrast to all other treatment methods, biological treatment is the only countermeasure that uses living organisms. All biosynthesized organic compounds can be degraded by microorganisms and by certain strains of bacteria and yeasts which play an important step in the carbon cycle. Their beneficial action has been incorporated in domestic wastewater treatment plants. However, for organic compounds that originate from man's synthetic activities alone and have been released in the environment, too short a time has elapsed to allow for the evolution of appropriate enzyme systems. This is very significant for halogenated hydrocarbons which are not naturally occurring compounds. (Gibson, et al., 1984)

The presence of bacteria in aquifer material, or the possibility to inoculate it by injection represents a definite advantage over all other methods to remove VOC's from groundwater. The contaminated water can be treated in situ, eliminating the risk for spills at the ground surface and the equipment capital costs are consequently lower. On the other hand, biodegradation is a slow process, and requires the addition of substrates which in themselves could create a contamination problem. For example, if nitrates are supplied to the contamination plume in excess to what is utilized, the difference may need to be removed from groundwater. The generation of toxic biodegradation products is a potential disadvantage when the treatment is not adequately controlled.

A study commissioned by the Petroleum Association for Conservation of the Canadian Environment has investigated the biotransformation of monoaromatic hydrocarbon constituents of gasoline. Two adjacent injections of 2500 litres of gasoline contaminated water with an average total aromatic hydrocarbon content of about 0.8 ppm were introduced below the water table into the shallow sand aquifer at Canada Forces Base Borden. Four days later, they were followed by two injections of 2400 litres of groundwater, upgradient from the contamination plume. Only one of the two latter volumes was spiked with nitrate: 44.9 ppm nitrogen (N) as nitrate (NO_3). An extensive sampling program was implemented and generated approximately 6000 samples in six "snapshot" sampling sessions at 8, 30, 79, 120, 160 and 300 days following the initial injection. Six components of gasoline, namely Benzene, Toluene, Ethyl benzene, p-Xylene, o-Xylene, and m-Xylene (BTEX) were monitored along with the dissolved oxygen content. After one month, the oxygen was depleted by aerobic bacteria and denitrifying bacteria took over the degradation process. As sorptive processes retarded the movement of BTEX, the nitrate plume swept it and produced a pattern of contamination distinctive to biodegradation: the decreased concentration of BTEX at the rear of the plume creates a fork-shaped distribution and the center of mass is deplaced to the front. (Berry-Spark, et al., 1986)

Biodegradation of chlorinated hydrocarbons has been tested in the United States and findings indicate that the product overall toxicity is not reduced. For example, anaerobic biodegradation of 1,1,1-trichloroethane and trichloroethene generates 1,1-dichloroethane and cis-dichloroethene as primary products (Parsons, et al., 1980; Fogel, et al., 1986). Further research is needed to resolve these anomalies and render a less toxic biodegradation product.

TABLE 6. GLOUCESTER CONCENTRATE ADSORPTION

Adsorbent	Dosage (g/L)	Equilibrium Concentration for Specified Organics (mg/L)							
		Benzene	Toluene	Ethyl Benzene	Dichloro-methane	Chloroform	Dichloro-ethane	Trichloro-ethane	Trichloro-ethene
Silicalite	0.110	7.63	4.72	0.2	0.05	0.07	1.47	0.06	0.56
	1.033	0.39	0.91	0.02	0.05	0.01	0.13	0.001	0.02
Imbiber Beads	0.105	7.97	1.75	0.07	0.15	0.06	1.35	0.16	0.76
	1.029	6.85	0.41	0.02	0.09	0.05	1.26	0.11	0.64
XAD-4	0.103	7.39	4.69	0.21	0.11	0.06	1.36	0.51	0.46
	1.007	2.07	0.87	0.02	0.05	0.04	0.67	0.03	0.14

Initial benzene concentration = 8.85 mg/L
Initial toluene concentration = .94 mg/L
Initial ethylbenzene concentration = .03 mg/L
Initial dichloromethane concentration = .16 mg/L
Initial chloroform concentration = .07 mg/L
Intital 1,1-dichloroethane concentration = 1.58 mg/L
Initial 1,1,1-trichloroethane concentration = .11 mg/L
Initial trichloroethene concentration = 1.22 mg/L

Resin Adsorption

As applied to VOC's, resin adsorption is very similar to activated carbon adsorption, the main difference being the substrate material. In this case, it is a synthetic instead of a processed naturally occurring organic. It is a technology which is seeing increasing use in industry. The costs are higher than for activated carbon, which is a disadvantage but some resins are available which will adsorb only the VOC's of interest while not adsorbing the much greater concentrations of naturally occurring organics. This gives the resins an advantage over carbon for the removal of VOC's from groundwater.

In a study conducted by Zenon Environmental Inc. for EETD, three synthetic adsorbents were tested on Gloucester Landfill groundwater which had been concentrated by a factor of ten times by reverse osmosis. The results, which are shown in Table 6, indicated that these resins would be applicable to removal of VOC's from that concentrated groundwater. (Zenon Environmental Inc, 1987)

Oxidation/Reduction

Oxidation/reduction reactions are those in which the oxidation state of one reactant is raised while that of another is lowered. It is primarily used for detoxification of cyanide and treatment of dilute contaminated groundwater containing oxidizing molecules. One of the major limitations is the formation of more toxic molecules through incomplete oxidation. Costs can vary greatly.

Although there have been some studies in the USA involving reduction of organics in groundwater, most Canadian and US studies have involved oxidation. In Canada, chemical oxidation, photochemical oxidation and electrochemical oxidation studies have been conducted in the recent past and/or are ongoing. One such study was conducted by WTC at the Gloucester Landfill in 1984. Air stripping, (AS), ozonation and UV photolysis of RO concentrate were studied at bench scale. (Simovic, et al., 1986)

Ozonation was studied in a 0.91 by 0.10 metre bubble column with ozone in the inlet and outlet gases being measured. The UV irradiation system consisted of four 9 watts mercury lamps emitting UV light at 254 nm. The results are shown in Table 7. Removal efficiencies observed after O_3 or UV irradiation alone were either similar to or lower than the results achieved with AS alone. Combinations of AS-O_3, AS-UV and O_3-UV unit processes compared to AS alone did not offer significant improvement in most tests, but, the combination AS-O_3-UV was better than AS alone.

TABLE 7. WTC 1984 AS-O3-UV RESULTS

Compounds	Range of Removal Efficiency (%)	Range of Residual Concentrations (ug/L)
Dichloromethane	89 - 99	7.1-45.5
Acetone	38 - 95	36.5-1933.8
1,1-Dichloroethene	29 - 99	0.5-45.4
Chloroform	87 - 99	6.2-2020.0
Diethyl Ether	84 - 99	0.7-95.0
1,2-Dichloroethane	63 - 99	1.6-56.5
Trichloroethene	99 - 99	0.5-3.5
Benzene	85 - 99	0.3-13.5

Steam Stripping

Steam stripping is similar to air stripping with steam being the working fluid instead of air. Both use a bubble tower or packed column. The technology enjoys wide usage in the chemical and petrochemical industries. Materials suitable for steam stripping include those with a low to medium boiling point and a low to medium solubility in water. This is typical of most VOC's.

The main advantage of steam stripping vis-â-vis air stripping is that steam is condensible allowing for the removal of VOC's for recovery and disposal in a concentrated form thus eliminating atmospheric emissions. The main disadvantage is the cost. Steam stripping can cost as much as $18.00 per 1,000 litres for a mobile system (including labour, electric power, fuel and maintenance).

Resource Conservation Company (RCC) in the US has developed a transportable steam stripper which has been used in some cleanups involving VOC's with very good results. In Canada, EETD has studied the development of a small, mobile steam stripper for use in environmental emergencies involving primarily VOC's. The computer generated results have been very encouraging (Table 8) and construction of the unit is planned for 1988. (CH_2M Hill, et al., 1987)

TABLE 8. STEAM STRIPPER PERFORMANCE ON SELECTED VOC's

Compound	Feed Flow(1) (L/Min)	Overhead(2) (% of Feed)	Ratio(3) (In/Out)	% Removal
1,1,1-Trichloroethane	37.9	10	7300	99.99
Benzene	37.9	10	6700	99.99
Ethylene Dichloride	37.9	10	6700	99.99
Methyl Ethyl Ketone	37.9	10	476	99.79
Methanol (Reflux = 25%)	30.3	20	100	99.0

1. All compounds except methanol were assumed to be present at ½ of their solubility limit at 25°C.
2. Overhead is the product stream exiting the top of the column.
3. Ratio is the ratio of contaminant in the feed to that in the bottoms.

TABLE 9. RESULTS OF ANALYSIS FOR 1986 TRIAL
MEAN VALUES

				MEMBRANE					
		CONCENTRATE		TORAY		FILMTEC		POST GAC	
CHEMICAL	PPB	PPB	% CONCENTRATED	PPB	% REJECTED	PPB	% REJECTED	PPB	% ADSORBED*
1,1-Dichloroethene	10.3	52.1	505	2.9	71.8	4.6	55.3	7.8	85.0
1,1-Dichloroethane	126.6	792.3	626	35.2	72.2	56.2	55.6	702.9	11.3
Diethyl Ether	273.6	1986.0	726	21.3	92.2	32.2	88.2	561.1	71.7
Chloroform	338.5	2312.5	683	49.0	85.5	81.9	75.8	261.1	88.7
1,2-Dichloroethane	128.2	748.2	584	33.7	73.7	55.0	57.1	133.1	82.2
1,1,1-Trichloroethane	144.9	1117.4	771	11.6	92.0	10.6	92.7	33.5	97.0
Trichloroethene	417.3	2090.8	501	99.8	76.1	180.2	56.8	16.2	99.2
Benzene	1177.4	9570.4	813	96.2	91.8	212.9	81.9	190.5	98.0
Toluene	204.5	1527.6	747	15.8	92.2	33.8	83.5	4.1	99.7
Chlorobenzene	8.2	24.9	304	4.7	42.7	2.7	67.1	3.5	85.9

* Includes periods in which breakthrough had occurred.

Reverse Osmosis

In reverse osmosis, pressure is used to drive water through a membrane while leaving inorganic and organic constituents behind. The precise level of rejection depends on the concentration, molecular shape and flexibility, size, ionic charge and solubility of a substance as well as the operating conditions and the membrane material. It is applicable to VOC contaminated groundwater solutions to the hundreds of ppm range. Problems can occur due to fouling, scaling and attack of the membranes by organic solvents at higher concentrations. pH adjustment and some prefiltering of suspended solids and oil and grease are necessary. The cost is comparable to that of activated carbon. RO is a concentration step which must be followed by further treatment of the concentrate.

EETD has carried out two studies at the Gloucester Landfill, (one 30 days and one 60 days). A total of 5 million litres of the VOC contaminated groundwater was treated in the two studies. In the 60 day study, GAC was used as a treatment step for the concentrate. The results of that study are summarized in Table 9. (Zenon Environmental Inc, 1987)

Solvent Extraction

Solvent extraction is a separation technique which involves two immiscible liquid phases. It is an indirect separation technique because two components are not separated directly. A foreign substance, an immiscible liquid, is introduced to provide a second phase. Contaminants that are preferentially soluble in the second liquid transfer to it until equilibrium is reached.

Solvent extraction is primarily applicable to concentrated streams such as those which frequently result from spills and leaking concentrated chemical landfills. It will seldom produce a treated effluent which does not require further treatment. The process is not naturally economically competitive with adsorption for very dilute solutions. Nevertheless it is a proven method of recovery.

Use in potential groundwater pollution remediation in North America is limited to sludge pit treatment by the Resource Conservation Company's (RCC) Basic Extractive Sludge Treatment (BEST). EETD has however, commenced a study of the use of this technology for concentrated VOC's in groundwater. A mobile unit is expected to be available in 1989.

The US EPA Treatability Manual lists the results for solvent extraction of VOC's shown in Table 10.

TABLE 10. SOLVENT EXTRACTION RESULTS FOR VOC's

Chemical	Concentration (PPM)	% Removal
Phenol	2,200,000	65
Benzene	11,000	90
Toluene	2,000	95
1,2-Dichloroethane	84,000	87
1,1,2-Trichloroethane	16,000	90

Pervaporation

Pervaporation is an emerging technology which has its roots in reverse osmosis and gas separation. In this instance, instead of a high pressure on one side of a membrane as is used in RO, the pressure gradient is generated by using low pressure, approximately 100 kPa (15 psi (g)) on one side of the membrane and a vacuum on the other. In the case of the recovery of VOC's, a hydrophobic membrane is used and the organics cross the membrane as a gas and are condensed on the vacuum side at low temperature.

Except for the dehydration of ethanol using hydrophilic membranes, most applications of pervaporation to date have been laboratory scale. In Canada EETD is carrying out a series of laboratory scale experiments using VOC's and hydrophobic membranes. Results to date include concentration of a 2465 ppm 1,2-dichloroethane solution to 650,000 ppm using a 2 mil low density polyethylene membrane. Experiments with other membrane materials and VOC's will be carried out shortly. On completion of the testing, a mobile pilot plant scale pervaporation unit, for use in spill cleanup, will be built.

The advantages and disadvantages of pervaporation are not yet known but it is expected that energy requirements may be high.

CONCLUSIONS

Contamination of groundwater by VOC's is a serious and growing problem. Many technologies, which have their roots in other industrial sectors have been investigated for remediation of this problem. This investigation is continuing as new technologies evolve and environmental regulations become more stringent.

Careful selection of the process(es) to be used is necessary. Errors can result in the formation of more toxic byproducts, failure to meet remediation standards or transfer of the pollution to another medium.

Canadian experience has covered a wide spectrum of technologies. Very good results have been obtained. Ongoing programs should ensure that even better results are achieved as newer technologies evolve and existing ones are optimized.

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Laboratory Scale Pervaporation Testing for Spills and Leachates

Diane Radnoff and Chris Lipski

Introduction

The process of pervaporation involves the differential diffusion of the components of a mixture through a membrane at different rates. This diffusion is governed by the membrane material, system parameters (such as pressure or temperature) and the nature of the components in the solution and their interaction with the membrane. A partial vacuum is often utilized on the downstream side of the membrane while ambient pressure is maintained on the upstream side. The liquid that is produced, referred to as the permeate, can be either stripped or enriched, depending on the type of membrane used. Although this method was employed during the early 1900's by pharmacists to dehydrate ethanol, little research has been conducted to date on pervaporation due to interest in other membrane separation processes such as Reverse Osmosis (RO).

Pervaporation can be used as a means of removing organic contaminants. This is achieved by contacting the upstream side of a hydrophobic membrane with the contaminated water while the downstream side is maintained at a vacuum below the vapour pressure of the permeate. As the contaminants diffuse through the membrane at a faster rate than water, they may be condensed and concentrated in the permeate. Pervaporation appears to be ideal for both the removal of highly concentrated (10% or more of organic compounds present) aqueous wastes that may cause damage to RO membranes and as part of a process train with RO where a stripped retentate is re-concentrated and then recycled by RO to the pervaporation system. A feed solution can often be enriched to the extent where the saturated permeate will undergo phase separation and can be either returned to a process or incinerated.

Pervaporation has several advantages over traditional treatment methods such as air stripping and carbon adsorption. Air stripping produces contaminated air that must be treated prior to discharge or a water pollution problem is simply turned into an air pollution problem. Carbon adsorption is limited in that the carbon can only adsorb a finite amount of the contaminants before it must be regenerated or disposed of, both of which can dramatically increase the cost of the treatment. With pervaporation, there is no limit to the degree of removal since the downstream side of the membrane is continuously evacuated. In addition, if pervaporation membranes become fouled, frequently they may be cleaned to recover their flowrates or to be re-used at another treatment site.

Theory

For a binary system, the pervaporation mechanism can be described by the Arrhenius relationship:

$$\ln Q = Ep/RT + Qo \qquad 1$$

where Ep = activation energy of permeation
R = gas constant
T = operating temperature
Qo = constant
Q = total flux

At low concentrations of a given component, the permeation rate of that component is proportional to its concentration in the mixture. At higher concentrations, enhancement or depression effects can often cause deviation from this proportionality. The nature of the components and of the membranes used will determine whether their interaction will result in enhanced or depressed permeation.

The selectivity (or separation factor) of a binary mixture can be expressed as:

$$\alpha_{B/A} = (YB/YA)/(XB/XA) \qquad 2$$

where YA, YB = concentrations of components A and B in the permeate
XA, XB = concentrations of components A and B in the retentate

As the system becomes more complicated, that is, the number of components in solution are increased, it becomes more and more difficult to describe the system with equations. At the same time, these equations begin to deviate further and further from the actual system performance. Presently, no equations exist that adequately describe a system containing more than two components; any available data is a result of experimental work and separation factors are derived empirically. Even the Arrhenius Equation, which describes the pervaporation mechanism, can only be used if the constant is derived through experimentation. (This is often even the case with binary systems. Solubility parameters can only provide an estimate of permeation rates and selectivities for a given membrane.)

Pervaporation is a method that is appropriate for the processing of organic/organic and organic/aqueous system due to the need to operate at the vapour pressure of the permeating components. This is not feasible with inorganic wastes as their vapour pressures tend to be extremely low. In addition, the removal of the bulk water would cause the retentate to become saturated in the salt such that the salt would precipitate out and foul the membrane.

Test Runs at the University of Waterloo, April 1987

Test runs were carried out at the University of Waterloo in Waterloo, Ontario, with a 2 mil low density polyethylene sheet (supplied by CIL). The cell is shown in figure 1. The membrane was used to effect the separation of low concentration ethylene dichloride (EDC) from water.

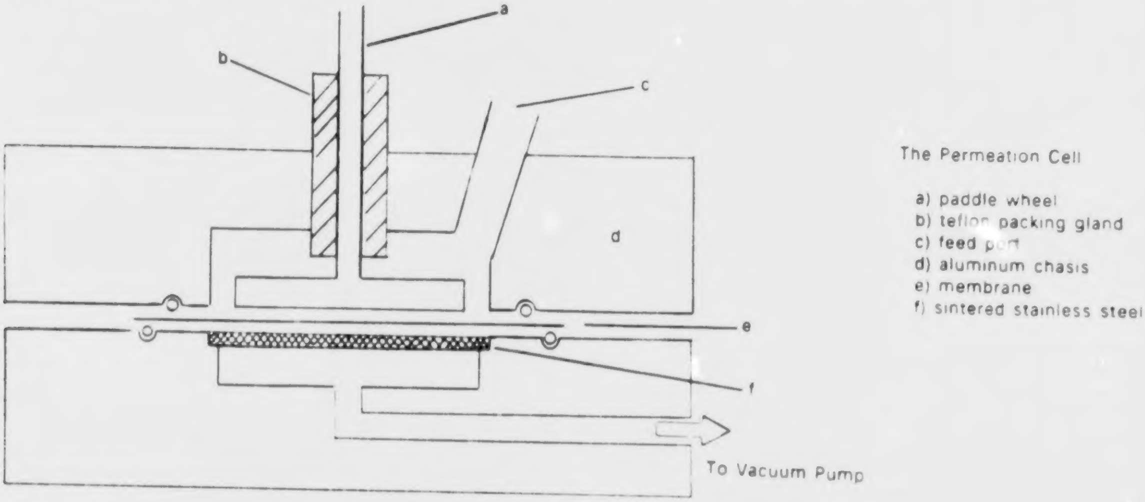

Figure 1: Permeation Cell

The surface area of the membrane was 0.007854 square metres. The operating pressure was approximately 1 mmHg and the temperature was maintained at 50 degrees celsius. The flux for a feed of pure EDC was estimated at 435 g/m^{2}h.

To condition the membrane for the first series of tests, it was stored in a saturated aqueous solution of EDC for 18 hours. Then the cell was charged with a solution containing 15,000 ppm EDC. For the second series of tests, the membrane was conditioned with a very dilute aqueous solution of EDC. The cell was subsequently charged with a 10,000 ppm solution of EDC. Permeate samples were taken twice during the first test series and three times during the second set of trials.

Results: Due to the limited number of trials, it was not possible to determine whether conditioning plays any role in the determination of the flux or the separation factor. Table I shows the fluxes and separation factors that were calculated following the trials. It is apparent that the concentration of the EDC in the permeate increased as the concentration of EDC in the feed decreased, not a common phenomenon for membranes. This can be explained in the following manner. The presence of the organic substance (EDC) would have caused the crystalline lattice in the membrane to swell, thus loosening the polymer and allowing water to more easily pass through the membrane. Therefore, as the concentration of EDC in the feed decreased, the water flux through the membrane also decreased. Thus, the drop in the water flux would be responsible for increasing the EDC concentration in the permeate. Once the EDC feed concentration is reduced to the extent such that the boundary layer on the liquid side of the membrane becomes the controlling parameter, its concentration in the permeate will also drop.

The overall flux rates indicate that polyethylene is a suitable material for the removal of EDC from water in concentrations above 1500 ppm. There may be other materials that would provide higher flux rates with comparable separation factors, but this is an area that would require further study.

Average feed Concentration (ppm)	Permeate Concentration (ppm)	Total Flux (g/m^2h)	EDC Flux (g/m^2h)	Water Flux (g/m^2h)	Separation Factor
4850*	181 000	738.75	133.71	605.04	45.35
3928*	364 000	157.75	57.42	100.33	145.15
4090	570 000	93.45	53.27	40.18	322.78
2935	561 000	50.00	28.05	28.05	434.12
2465	650 000	39.99	25.99	14.00	751.55

Table I: Results from EDC Trials at Waterloo

*Results from the first test series

Pervaporation Field Trial, December 1986

Pervaporation trials were conducted at Gloucester landfill with a B9 Permasep® Permeator from Dupont. This membrane is an aramid polymer with a hollow fiber configuration in a filament wound fiberglass epoxy shell. It is shown in figure 3.

The system consisted of the membrane with a vacuum pump connected to it on the downstream side. The permeate was collected in an Erlenmeyer flask. The feed to the system was leachate from the landfill. Samples of the feed, permeate and retentate were collected at various intervals and analyzed by a Model 5830 Hewlett Packard Gas Chromatagraph.

Samples of the permeate exhibited some enrichment of some of the organic components. However, since no cold trap was used to aid in the condensation of the organic vapours, it was believed that much of the vapour was lost to the atmosphere when sampling was conducted. Therefore, it was decided to conduct the trial again, at a later date with the Erlenmeyer flask used for permeate collection in a cold trap.

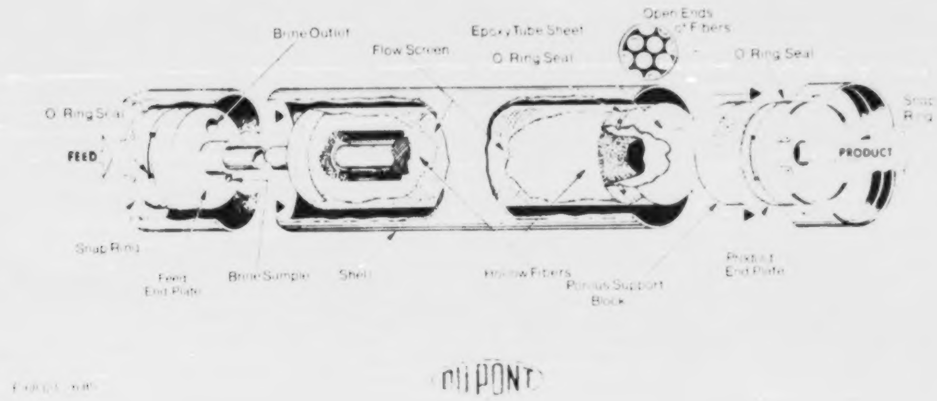
Brine Outlet
Epoxy Tube Sheet
Open Ends of Fibers
Flow Screen
O Ring Seal
O Ring Seal
O Ring Seal
Snap Ring
FEED
PRODUCT
Snap Ring
Feed End Plate
Brine Sample
Shell
Hollow Fibers
Porous Support Block
Product End Plate
DUPONT

Figure 3: Dupont B9 Permasep^R Permeator

Pervaporation Field Trial, June 1987

In June of 1987, field testing was done with pervaporation at the Gloucester Landfill. The system setup is shown in figure 4. The membrane utilized in this case was the B10 Permasep^R Permeator from Dupont. It has a similar configuration and polymer composition to the B9 module.

In order to achieve a greater separation of volatile materials, the landfill leachate used in the testing was first concentrated by a factor of 8:1 by Reverse Osmosis. However, the 400 L of concentrate produced by this method had to be stored outside where temperatures averaged 25 degrees celsius daily. Therefore, 500 mL of a spiking solution was added each day to the tank. This was done to restore the concentration of the test solution back to that of the RO-produced concentrate. The spiking solution contained chemicals present in the landfill leachate, including:

1,1-dichloroethane
1,1-dichloroethene
1,1,1-trichloroethane
diethylether
benzene
hexane
toluene
chlorobenzene
chloroform

In addition, there are high concentrations of calcium carbonate present in the Gloucester leachate. To avoid membrane fouling, Hydrochloric acid was added to the feed to bring the pH down to between 5 and 6. The temperature of the solution was maintained at 37 ± 5 degrees celsius during the trials.

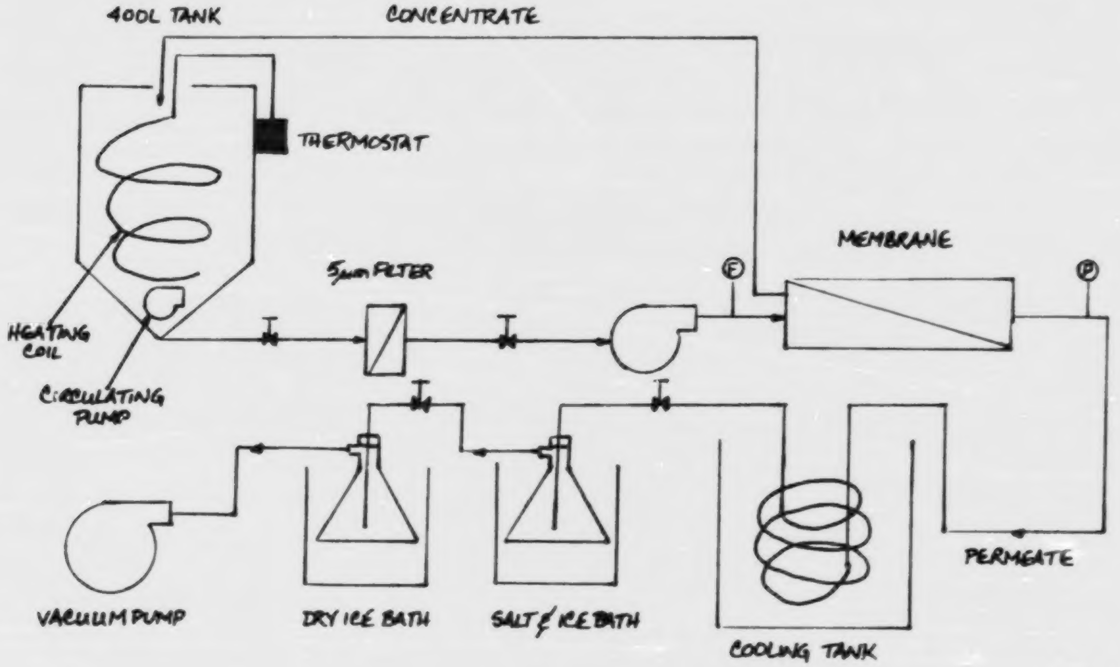
400L TANK
CONCENTRATE
THERMOSTAT
MEMBRANE
5μm FILTER
Ⓕ
Ⓟ
HEATING COIL
CIRCULATING PUMP
VACUUM PUMP
DRY ICE BATH
SALT & ICE BATH
COOLING TANK
PERMEATE

Figure 4: Pervaporation System

Test Procedure: The temperature and pH of the test solution were measured and adjusted if necessary. The feed pump was then started and the flowrate of the feed to the membrane was regulated to the desired level, (2.0, 3.0, 4.0, 5.0 and 7.0 L/min). The vacuum pump was then started up and allowed to operate continuously throughout the entire run to achieve the maximum vacuum possible. The duration of each run was one hour; samples of the permeate collected in each Erlenmeyer were taken and the amounts collected were recorded. The pH and conductivity of the permeates were also measured and compared with those of the feed.

Results: The following data, shown in table II, was collected during the trials; the lines dividing the measurements denote data collected on different days. There was no data for the permeate collected in the second Erlenmeyer as only 1 mL of liquid (or less) condensed there. Primarily organic vapours were transferred to the second Erlenmeyer as the temperature in the first Erlenmeyer was not low enough to allow some of the organic components to condense when the system was under vacuum. At the lower temperature in the second Erlenmeyer, the vapour froze instantly. This was evident by the presence of a frozen residue on the sides of the Erlenmeyer. However, when the Erlenmeyer was allowed to come to room temperature for sample collection, these organic compounds vapourized and were lost. Thus, when the flask was opened to collect the small amount of liquid present, the organic vapours would have been lost to the atmosphere.

Run	Feed Flow (L/min)	Feed Temp (°c)	Conduct Feed (µmhos)	Feed pH	Amt Perm (L)	pH Perm	Conduct Perm (µmhos)	Avg Vacuum (inHg)
1	2.0	35.0	5500	4.0	0.75	5.7	1900	23.0
5	4.0	31.0	4700	5.6	0.75	5.5	2000	24.0
6	4.0	38.0	5000	5.8	1.00	5.8	2000	24.9
7	4.0	41.0	5100	6.1	1.00	5.8	2100	23.2
8	6.0	38.0	5000	6.2	1.00	5.8	2100	23.5
9	5.0	38.5	5300	6.4	1.00	5.7	1900	23.3
16	5.0	40.0	6000	5.7	1.25	5.9	2100	24.0
17	5.0	41.0	6000	4.7	1.10	5.9	1900	24.0
18	7.0	42.0	6000	5.9	1.40	5.1	2000	24.0
19	3.0	41.0	5800	5.1	0.80	5.6	1900	24.5

Table II: Data from Gloucester Trials (June)

It is obvious that both the feed flowrate and the operating vacuum pressure on the system have an effect upon the amount of permeate that was collected. Of the two, the vacuum appears to have the greatest effect as a higher vacuum will tend to "pull" more liquid through the membrane. More testing should be done in this area to determine exactly the magnitude of the effect of variations in the vacuum pressure on the system. (It should be noted here that this effect will be dependant on the type of membrane being used. With some membranes, a high vacuum may cause the membrane to dry out and restrict the flow across the membrane.) Fluctuations in the feed temperature could also affect the system, however, the temperature varied by no more than 26% between runs. In this case, the magnitudes of the variations would not seriously influence the flowrates.

Of major concern here is how the changing of system parameters affected the concentrations of the organic substances in the permeates. Unfortunately this, and the effect of the use of the two traps (one with ice and salt and one with dry ice) cannot be examined here as the analysis of the samples is still in progress. This information will be reported at a later date.

Acknowledgements

The writers would like to thank Charles Goulet for the assistance he provided during the pervaporation field trials at Gloucester Landfill, both in December 1986 and in June 1987 and Robert Huang at the University of Waterloo for the use of his permeation cell and vacuum pump.

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MOBILE STEAM STRIPPER AS AN ENVIRONMENTAL EMERGENCIES COUNTERMEASURE

Gary Giesbrecht - CH2M HILL ENGINEERING LTD.
Francine Laperriere - Environment Canada
Daniel Peterson - Resources Conservation Company

INTRODUCTION

This paper outlines the feasibility of using a mobile steam stripper for removal of volatile organic compounds from contaminated groundwater. It is based on a study carried out by CH2M HILL and Resources Conservation Company for the Environmental Emergencies Technology Division of Environment Canada.

The need for such a unit is discussed along with the constraints expected in actual use. The physical characteristics that make a compound amenable to steam stripping are discussed and a preliminary list of candidate compounds presented. A conceptual design is described and the expected performance on selected compounds is outlined.

BACKGROUND

For the past five years, the Environmental Emergencies Technology Division has been involved in development of countermeasures for chemical spills. The first technology which was investigated was reverse osmosis (RO). This technology has been very successful in several tests and cleanups of fairly dilute solutions but it is not capable of treating spills of halogenated aliphatic compounds.

The need for environmentally acceptable countermeasures for that family of chemical compounds and for larger concentrations of chemicals was brought into focus when several requests for assistance were turned down.

In February 1986 a Canadian National Railways freight train partially derailed at Fort Langley, B.C. It resulted in a 336 000-litre ethylene dichloride spill on a sandy soil. Contamination of the groundwater occurred. At the centre of the plume, which was hundreds of metres long, the product was at a concentration of about 1-2 percent. RO cannot be used at this concentration level. At the edge of the plume the concentration was down to 100-1,000 ppm. The only possible cleanup technique was to pump several hundred thousand litres of this solution to the surface for treatment and to air strip the more dilute regions of the contaminated groundwater plume.

Following discovery of organically contaminated spring runoff at a landfill in Sarnia, Ont., an assessment of a large-scale carbon treatment facility was done for the removal of halogenated hydrocarbons from an effluent. Volatiles such as PCE, EDC, CTC, 1,1 Dichloroethane, and 1,1,2 Trichloroethane were present in low ppm levels up to 100 ppm. RO assistance would not have improved the overall efficiency of the treatment, RO being less efficient than the carbon bed for the removal of 1,2 Dichloroethane but more efficient than carbon for the removal of 1,1 Dichloroethane. Other compounds removal efficiency with carbon is comparable to RO removal efficiency.

An assessment of cost-effective technologies for the treatment of aqueous effluents from in situ heavy oil recovery was initiated two years ago by

Environment Canada. These effluents contain a few thousand ppm of dissolved organics and inorganics and RO could not be included in the study.

The Environmental Emergencies Technology Division has now started a program of developing several processes to deal with spills of chemical compounds such as the halogenated aliphatics. The object is to develop several processes which can be brought to the site of a chemical spill and used in series so that no contaminated material leaves the site with the exception of recovered concentrated chemical to be sent for reprocessing. These processes could also be applicable to remediation of leaking chemical landfills.

One of the technologies looked at by Environment Canada is steam stripping. It is meant to be used as the first step of the chemical concentrating process. It should handle solutions of 1-2 percent and provide a more concentrated stream to solvent extraction and distillation processes. The resulting aqueous phase could be further treated by RO if needed.

PREVIOUS WORK

The first part of the feasibility study was a review of the current literature to determine the extent of similar previous work.

No publications were found that dealt with actual operation of steam stripping on priority pollutants although there were a few that predicted success based on a review of physical properties. Steam stripping is widely practised in the petroleum industry for removal of acid gases and in the pulp and paper industry for removal of organics and toxicity. Unfortunately, the pulp and paper publications generally express concentrations in terms of BOD or COD which do not translate well from one application to another.

Considerable work on air stripping of volatile organics has been published. The mass transfer aspects of air stripping are similar enough to steam stripping to view the data positively.

In summary, previous work on the subject is encouraging but lacking in detail.

STEAM STRIPPING BASICS

Steam stripping is a separation process that makes use of differences in the thermodynamic properties of the compounds to be separated. The stream to be stripped is heated and contacted with a vapour phase that is successively leaner in the compound being stripped. If the vapour pressure of the compound being stripped is sufficiently high relative to water, it can be removed to very low levels.

In actual operation, the process is normally carried out in a vertical column fitted with trays or packing to enhance vapour/liquid contact. Steam is introduced at the bottom and passes upward through the column. The water to be treated enters at the top and flows down to the bottom. Thus the lowest concentration water is contacted with the lowest concentration steam and the highest concentration water is contacted with the highest concentration steam. The steam source may be either direct steam injection or from indirect heat transfer in a reboiler. The overhead vapour is condensed and a portion may be returned to the top of the column as reflux. If the overhead stream is a two-phase mixture after condensing, a decanter is used to separate the stripped compound from the water phase. A schematic diagram of a generalized stripping column is shown in Figure 1. The water flowing from the feed point down toward the outlet becomes progressively leaner and the vapour phase becomes progressively richer as it flows upward. This section is called the stripping section and in most cases is all that is required. If there is a mass transfer zone above the feed point, the liquid source is returned as overhead product or reflux. Again, the liquid becomes progressively leaner and the vapour progressively richer. This section is called the rectification section and is used to increase the concentration of the overhead product.

The configuration described above is similar to other mass transfer operations such as distillation and gas scrubbing. One unique aspect of steam stripping is the effect of solubility on the vapour/liquid equilibria of aqueous solutions. The vapour/liquid equilibrium of a binary mixture can be represented by a temperature-composition diagram. Typical diagrams are shown in Figures 2 through 4. In each diagram the upper line represents the vapour composition and the lower line the liquid composition. Vapour and liquid mixtures in equilibrium with each other are joined by horizontal lines. An ideal mixture is similar to that shown in Figure 2. Note that the vapour phase is always richer in the compound with the lower boiling point. Thus a pollutant that is less volatile than water and forms an ideal or nearly ideal mixture with water cannot be economically removed from water by steam stripping. Figure 3 represents the vapour/liquid equilibrium of a mixture that is so non-ideal that it forms an azeotrope. In this case since there is a low boiling azeotrope, dilute solutions of the pollutant can be stripped even though it is less volatile than water. A special case of azeotrope occurs in systems where the compounds are only slightly soluble in each other. In these systems in the two-phase region each compound exerts its own vapour pressure and forms what is called a heteroazeotrope. A typical equilibrium diagram is shown in Figure 4. As long as the initial concentration is more dilute than the azeotrope concentration, the compound is a good candidate for steam stripping.

Equilibrium relationships for binary systems, such as an organic contaminant in water, can be characterized by the relative volatility. An ideal relative volatility can be defined as the ratio of contaminant vapour pressure to water vapour pressure at a given temperature. As the relative volatility approaches the value of one, the potential to strip that compound diminishes. Ideally, this would imply that the vapour pressure of the contaminant would always have to be greater than water. However, AquaDetox technology takes advantage of the fact that compounds are not ideal and that azeotropes distort the ideal relative volatility, providing the potential for stripping.

The other factors which are incorporated into the relative volatility are the solubility of water in the component and the solubility of the component in water. If the compound is readily strippable and exhibits low solubility characteristics, the compound will be readily removed and concentrated by the AquaDetox steam stripping process with a minimum amount of steam.

Using AquaDetox technology, one can steam strip about 80 percent of the chemicals on the USA EPA-designated Priority and Appendix VIII Pollutant list, most of which are non-ideal. Examples of these chemicals are shown in Table 1.

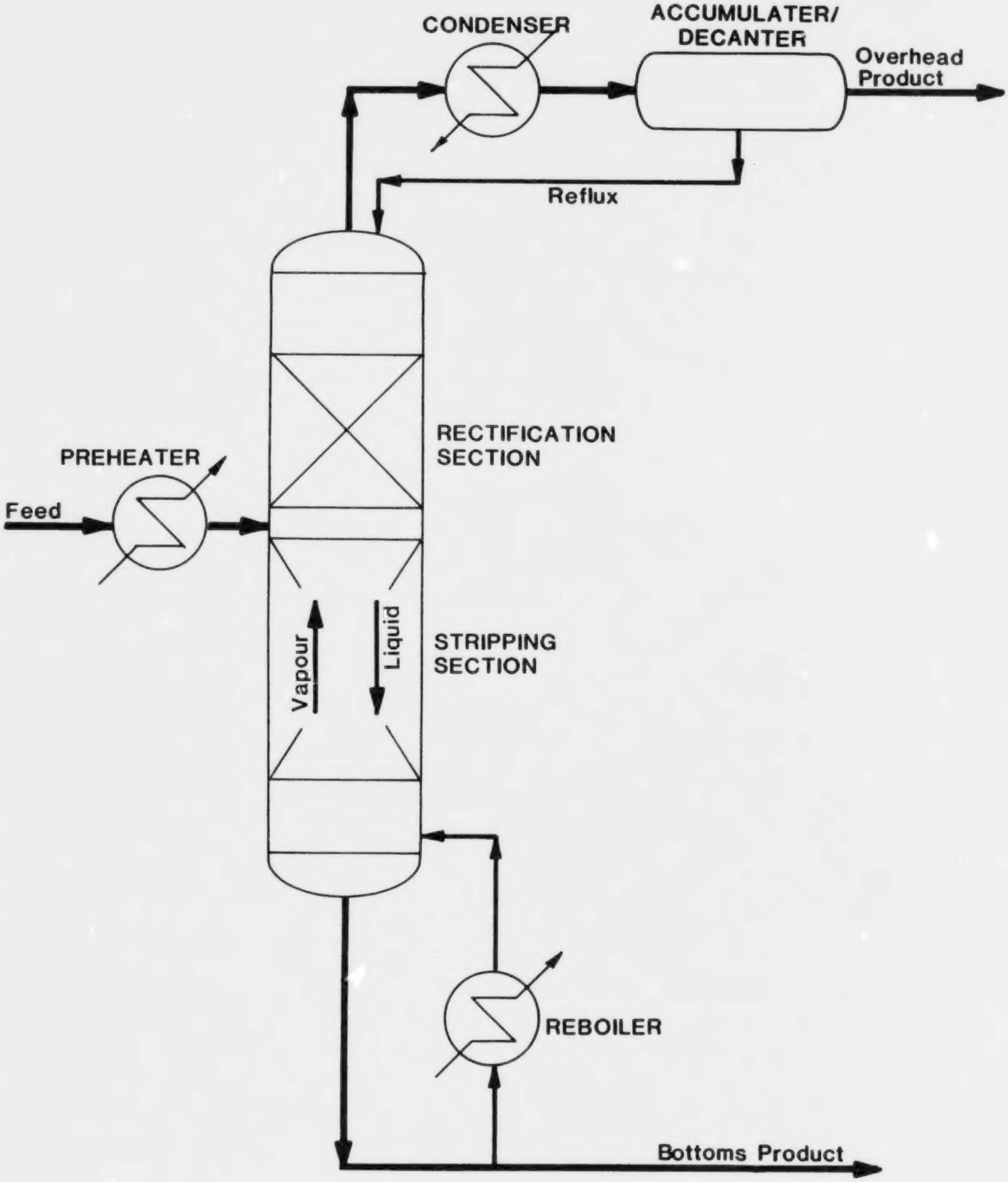

CONDENSER
ACCUMULATER/
DECANTER
Overhead
Product
Reflux
RECTIFICATION
SECTION
PREHEATER
Feed
Vapour
Liquid
STRIPPING
SECTION
REBOILER
Bottoms Product

Figure 1
SIMPLIFIED PROCESS SCHEMATIC

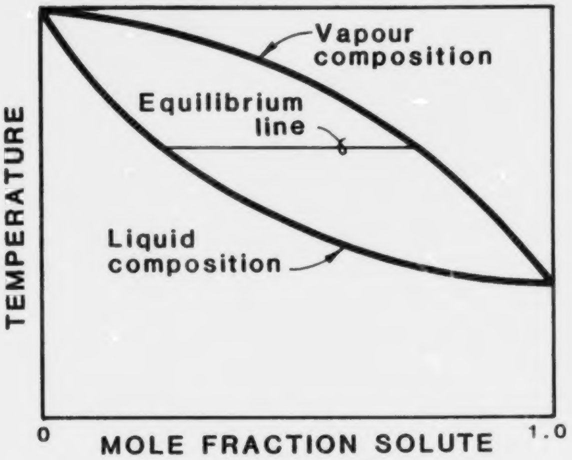


Figure 2
IDEAL MIXTURE

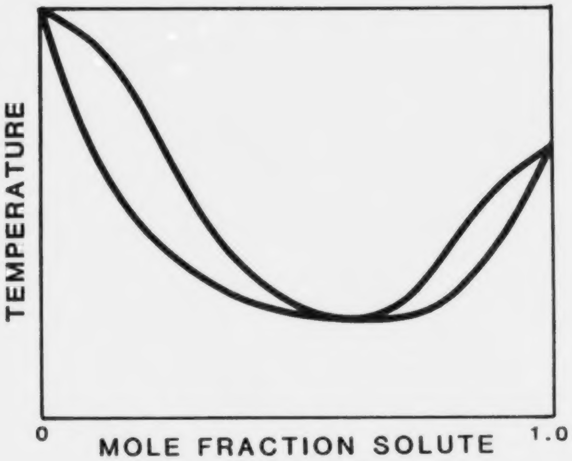


Figure 3
LOW BOILING AZEOTROPE

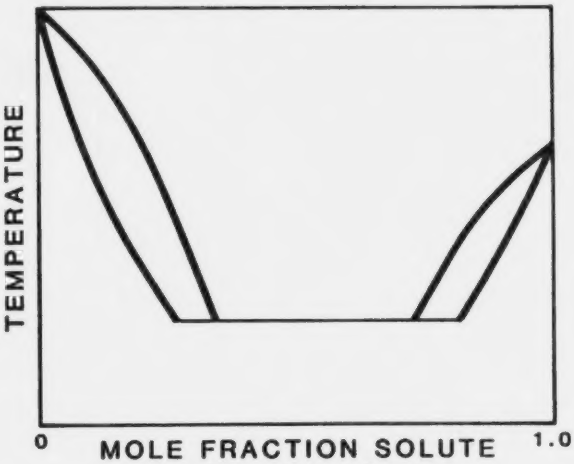


Figure 4
HETEROAZEOTROPE

Table 1
A PARTIAL LIST OF STRIPPABLE EPA-DESIGNATED PRIORITY
APPENDIX VIII POLLUTANTS

Chloroethane
1,1 Dichloroethylene
Methyl Chloride
Methyl Bromide
Trichlorofluoromethane
Dichlorodifluoromethane
Vinyl Chloride
Chrysene
Acenaphthalene
Anthracene
Fluorene
Phenanthrene
Pyrene
Tetrachloroethylene
Toluene
Trichloroethylene
Aldrin
Chlordane
4.4 - DDT
Heptachlor
Biphenyl
2-Chlorobiphenyl
2,2-Dichlorobiphenyl
Trichlorobiphenyl
Tetrachlorobiphenyl
Pentachlorobiphenyl
Toxaphene
2,3,7,8-Tetrachlorodibenzo-P-Dioxin (TCDD)
Acenaphthene
Acrolein
Acrylonitrile
Benzene
Carbon Tetrachloride
Chlorobenzene
1,2,4 Trichlorobenzene
Hexachlorobenzene
1,2-Dichloroethane
1,1,1-Trichloroethane
Hexachloroethane
1,1 Dichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
2-Chloroethylvinyl Ether
Chloroform
1,2-Dichlorobenzene
1,2-Trans-Dichloroethylene
1,2-Dichloropropane
Ethylbenzene
Fluoranthene
Bis (2-Chloroisopropyl) Ether
Bis (2-Chlorethoxy) Methane
Methylene Chloride
Bromoform
Dichlorobromomethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Napthalene
Nitrobenzene
Pentachlorophenol

AQUADETOX DATABASE

The AquaDetox database developed by Dow Chemical Company consists of many organic compounds (some inorganic as well) which are classified as follows:

- Glycols
- Alkanol Amines
- Amides
- Acids
- Phenols
- Alcohols
- Glycol Ethers
- Primary and Secondary Amines
- Nitriles
- Aldehydes
- Ketones
- Esters
- Oxides
- Tertiary Amines
- Sulfoxides and Sulfones
- Halogens
- Aromatics
- Paraffins and Sulphides
- Various Miscellaneous Compounds

The following data are available:

- Equilibrium information (liquid and vapour)
- Activity coefficient
- Relative volatility
- Physical properties

AQUADETOX STEAM STRIPPING EXAMPLES

Testing of water is an all important part of determining whether or not steam stripping is applicable. For instance, data available on compounds are generally for pure components in water at a given temperature, say 20°C or 25°C. Extrapolation of this data to 100°C or assuming that a mix of components will behave as if they were pure may not be valid. Testing on a small scale will provide the data necessary to design a full-scale column. Several tests, using a 1 gph laboratory stripper, have been run to provide data.

A test involving ethylene dichloride, acetone, and methanol was run. Testing showed that the combination of components could be removed by steam stripping. However, since methanol (major component) is miscible with water and does not phase split from the foul condensate,the foul condensate stream was relatively large. In order to reduce the waste flow, a rectification section was added to the design. The rectifier receives overhead vapour from the stripping section and reduces the foul condensate stream by about a factor of five in volume. The rectifier returns about 80 percent of the original foul condensate from the stripper as water at about the same concentration as the original feedwater to the stripper. Table 2 shows the test results (stripping section only) with expected performance in a full-scale stripping column.

Table 2
AQUADETOX TEST - CHEMICAL PLANT WASTE
ETHYLENE DICHLORIDE/ACETONE/METHANOL

	Test Unit	Full Scale
Feed Flow Rate, lb/hr	10	17,000
Feed Concentration, ppm		
Ethylene Dichloride	297	297
Acetone	358	358
Methanol	736	736
Treated Water Concentration, ppm		
Ethylene Dichloride	£5	£1
Acetone	£5	£1
Methanol	6	£1
Overhead Steam Rate, % of Feed	17	15

Another recent test examined AquaDetox steam stripping a groundwater contaminated with PCP. Prior to being steam stripped, the water containing PCP must be acidified to convert PCP to the non-ionized form. (Ionized molecules in general cannot be removed by stripping processes.) PCP is quite soluble in the ionized form but is only about 10 ppm soluble at low pH. For this case, acidification produced a precipitate of PCP since the initial concentration was about 16.4 ppm. The feed was then filtered prior to being introduced to the stripping column. Table 3 shows the resutls of ADTU testing and the predicted performance of a full-scale column based on test results. PCP can be reduced to levels of less than 5 ppm by AquaDetox steam stripping based on the test results.

Table 3
AQUADETOX TEST - CONTAMINATED GROUNDWATER
PENTACHLOROPHENOL

	Test Unit	Full Scale
Feed Flow Rate, lb/hr	11	50,000
PCP in Feed, ppm*	10	10
PCP in Bottoms, ppm	0.03	<0.005
Overhead Steam Rate, % of Feed	13.5	15

* After acidification. Prior to acidification, the PCP concentration was 16.4 ppm.

DESCRIPTION OF PROPOSED EQUIPMENT

Design Basis

For a mobile steam stripper to fulfill its intended function, it needs to be:

- Mobile. It must be transportable by conventional and medium duty trucks.
- Flexible. It must be able to function on a variety of compounds at varying concentrations in real situations.
- Rugged. It must withstand the rigours of transport, assembly, and disassembly.
- Easy to use. In some situations, speed of response may be critical. The unit must be easy to set up, easy to start up, and easy to operate.

In designing a fixed industrial installation, the usual approach is to determine the required flow and performance and then design the column to suit. For this application, both the flow and the inlet/outlet concentrations are either variable or not subject to firm requirements. Rather than trying to develop a set of performance criteria for a system that, realistically, will have to handle a wide variety of conditions, the approach taken was to size the equipment to meet the shipping and setup constraints and then calculate its performance in a number of selected situations.

A number of constraints were set as a basis for developing the conceptual design. These constraints were based on Environment Canada's preferred method of operation. First of all, the complete system, excluding tankage, is to fit in a two- or three-ton GVW box van of the type commonly available at rental agencies. This results in a dimensional limit on the equipment in the shipping mode of 2100 mm x 2100 mm x 4800 mm. The equipment must be able to be unloaded and set up using rental equipment that would normally be available even in moderately small centres. The system must be able to be assembled using no more than a three-person crew in not more than 24 hours. The number of utilities required is to be an absolute minimum. Foundation requirements are to be limited to a prepared gravel pad.

With these constraints in mind, the preliminary design described below was developed.

Process Description

The system consists of two key process elements, a packed stripping column (305 mm diameter x 6 m packed height) and an overhead accumulator/decanter. A low pressure package boiler is provided to supply the necessary steam. Cooling water was not expected to be available as a matter of course so that all heat rejection is by an air-cooled condenser. In order to minimize both the boiler size and the condenser size, a number of small exchangers are included to optimize heat recovery. Since many of the compounds considered for stripping have very low boiling points, it was considered necessary to subcool the overhead product to prevent excessive vapour loss. In addition, since some compounds are highly toxic, an activated carbon filter is provided on the decanter vent.

The process flow diagram is shown in Figure 5. Feedwater is pumped from a storage tank through the overhead subcooler and then, together with the return aqueous phase from the decanter, to the stripping column. These two streams may be heated and returned separately if it is judged desirable to use part of the column as a rectification section. The water being stripped flows down the column while steam is introduced at the bottom and travels upward. The compound being stripped is concentrated in the vapour phase which then passes through an air-cooled condenser and the subcooler to the decanter. The separated aqueous phase is returned to the column while the decanted hydrocarbon phase is pumped to a waste tank. Treated water is pumped from the bottom of the column through the feed heater to a storage tank.

Only two control loops are included, the liquid level in the lower section of the column and the interface level in the decanter. Both of these are rugged, float-actuated valves.

In order to enable adequate heat rejection from the condenser even in hot weather, a water spray is provided to wet the air side surface and increase the temperature driving force.

A key part of the system is a microcomputer-based simulation program which will allow calculation of the optimum feed and steam rates, feed point, and feed heater configuration for each situation the system is required to handle. This would normally be done while the system is in transit and being set up.

Mechanical Description

The equipment is divided into two main modules, a process module and a boiler module. The upper column sections and boiler stack are nested on the top of the boiler module for shipment and assembled in the field. The air-cooled condenser is nested on the process module and set adjacent to it for operation. The process module contains the lower column section, heat exchangers, and pumps. The upper column sections are connected by light duty

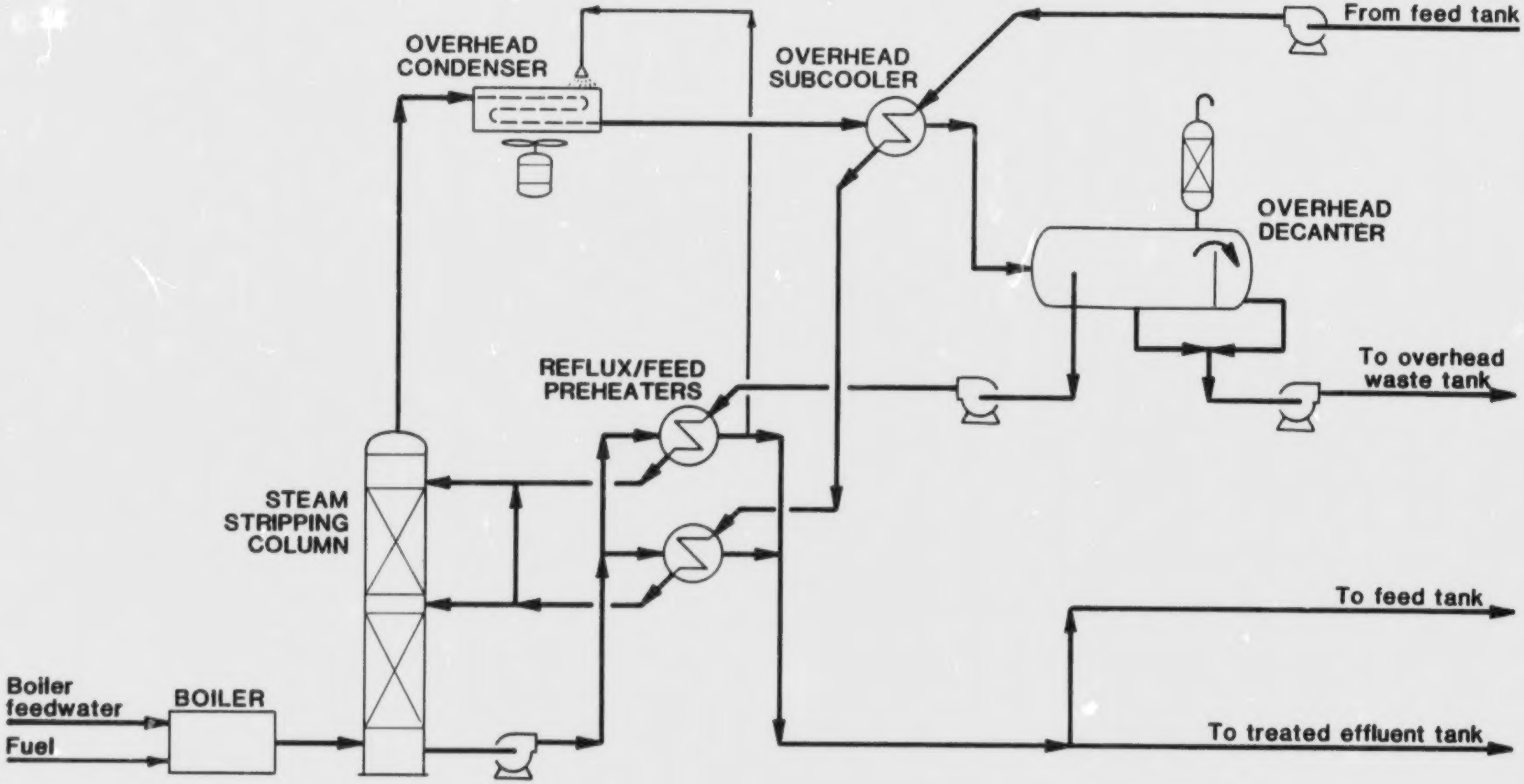

From feed tank
OVERHEAD CONDENSER
OVERHEAD SUBCOOLER
OVERHEAD DECANTER
To overhead waste tank
REFLUX/FEED PREHEATERS
STEAM STRIPPING COLUMN
To feed tank
Boiler feedwater
BOILER
Fuel
To treated effluent tank

Figure 5
MOBILE STEAM STRIPPER
PROCESS FLOW SCHEMATIC

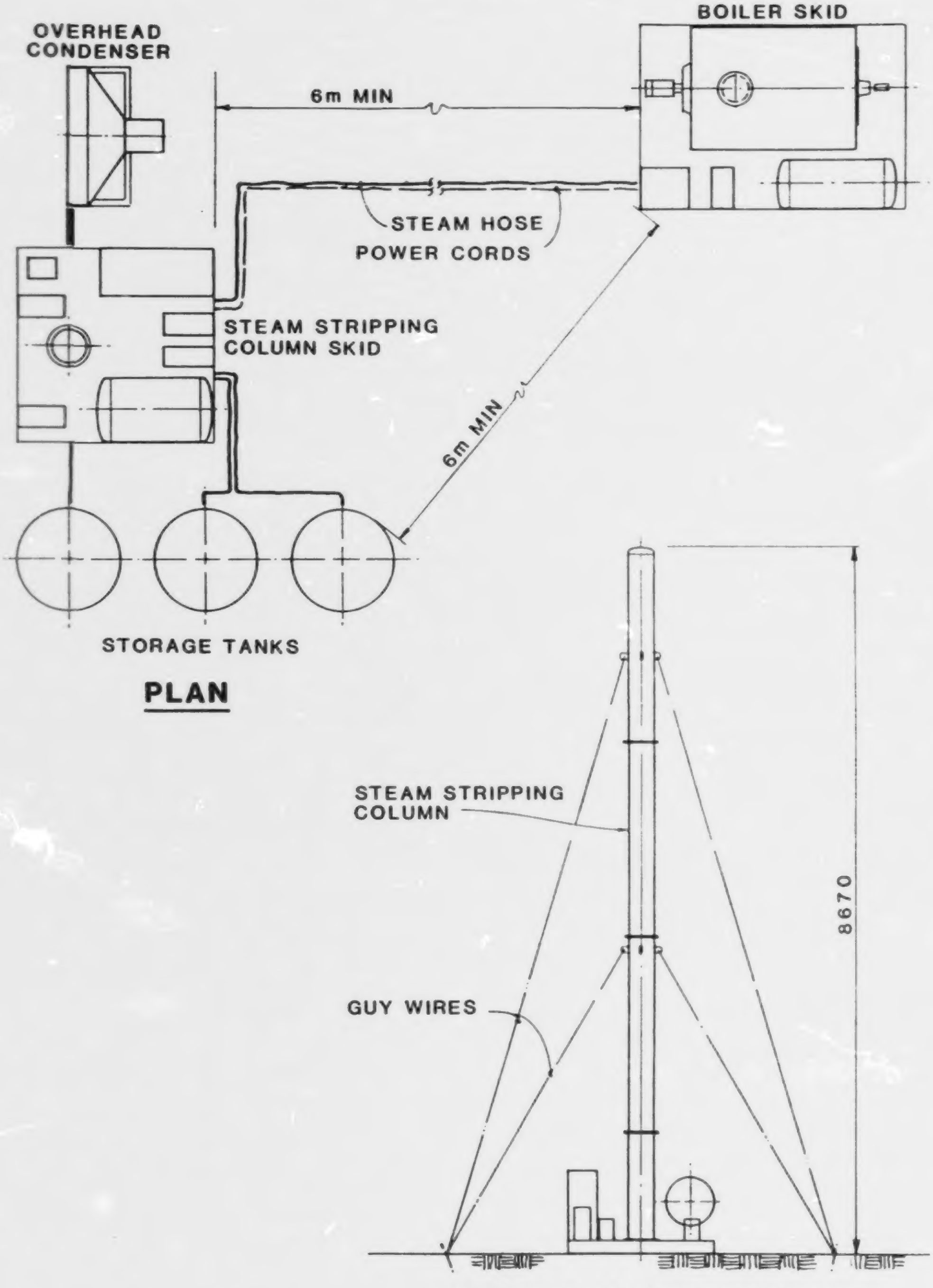
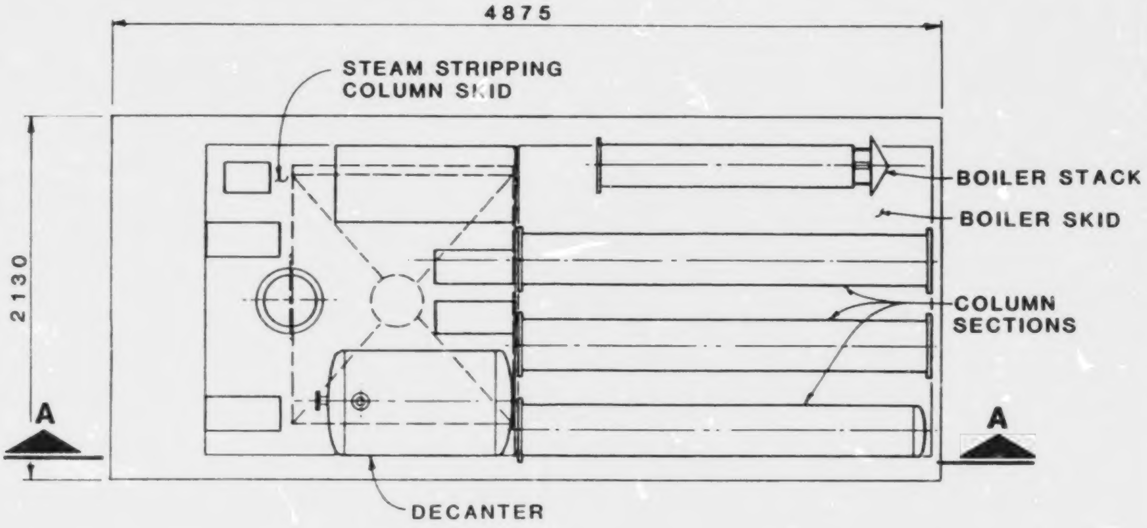
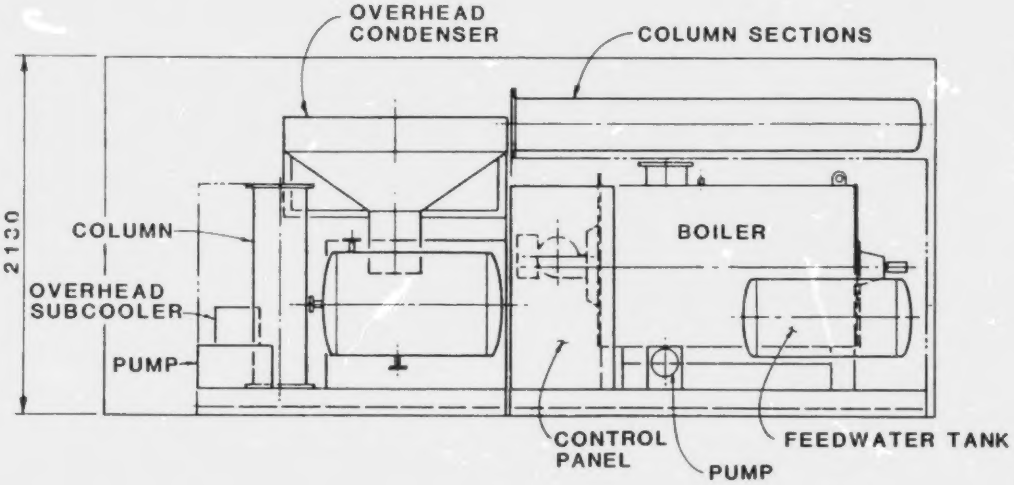

OVERHEAD CONDENSER
BOILER SKID
6m MIN
STEAM HOSE
POWER CORDS
STEAM STRIPPING COLUMN SKID
6m MIN
STORAGE TANKS
PLAN
STEAM STRIPPING COLUMN
8670
GUY WIRES
ERECTED CONFIGURATION

Figure 6
OPERATING


4875
STEAM STRIPPING COLUMN SKID
BOILER STACK
BOILER SKID
COLUMN SECTIONS
2130
A
A
DECANTER

PLAN


OVERHEAD CONDENSER
COLUMN SECTIONS
2130
COLUMN
OVERHEAD SUBCOOLER
PUMP
BOILER
CONTROL PANEL
PUMP
FEEDWATER TANK

SECTION A-A

Figure 7
SHIPPING

CH2M HILL

flanges and have the feed and overheads lines attached to them and fitted with quick-connect couplings at each end. The boiler module includes a package fire tube boiler and all of the system controls and motor starters.

Due to the possibility of hydrocarbon vapours, the process module would be classified hazardous electrically. A minimum distance of 6 metres is required between the two modules. Mounting the controls on the boiler module avoids the expense of an explosion-proof panel.

The stripping column is assembled in three sections above the process module. Guy wires anchored with driven stakes provide vertical stability. Tankage for the column feed, treated water, and recovered hydrocarbon and interconnecting hoses and power wires complete the system.

Figures 6 and 7 show the proposed system in the operating and shipping modes respectively.

Expected Performance

A preliminary list of candidate compounds was drawn up by Environment Canada at the beginning of the study. A review of the physical properties of the initial list of compounds resulted in a few modifications to the list and enabled the selection of a short list that was representative of the range of physical properties in the complete list. The final list of compounds considered is shown in Table 4 along with selected physical properties. This list is not a list of all compounds that can be removed from water by steam stripping. Rather, it is a list of compounds that are both considered to constitute an environmental risk and to be suitable for steam stripping.

Table 4
LIST OF CANDIDATE COMPOUNDS

Candidate Compound	Molecular Weight	Vapour Pressure kPa	at Temp. (C)	Henry's Law Constant @ 25C (mta-m^3/mole)	Solubility (g/100g)	Boiling Point (C)
Formaldehyde	30	100.00	-19.5		miscible	-20
Butyraldehyde	72	9.40	20	7.1	75	
Acetone	58.08	51.50	100	6.80E-06	230	56.2
Methyl Ethyl Ketone	72.11	10.30	20	2.40E-05	35.3	79.6
Methyl Isobutyl Ketone	100.16	1.30	30	1.32E-04	1.9	119
Methanol	32.04	21.20	30	1.10E-06	440	64.5
Ethanol	46.1	10.00	30		miscible	78.4
Isopropanol	60.1	7.60	30		miscible	83.4
Butanol	74.12	1.3-7.5	30	7.00E-06	9.1	83-118
2-Ethyl Hexanol	130.2	0.13	33		0.1	179-185
n-Hexane	86.17	20.20	25	1.23E+00	0.00095	68.7
Forsic Acid	46	7.00	30		miscible	100.8
Methylanine	31-59	192-313	20		miscible	-6.5-2.9
1,3 Butadiene	54.1	281.00	25	7.38E-02	0.074	-4.4
Acrylonitrile	53	196.00	100		7.3	77.4
Methyl Methacrylate	100.1	6.50	30		1.5	100
Cyclohexane	84.16	12.70	25	1.78E-01	0.005	80.7
Benzene	78.11	187.00	100	5.55E-03	0.18	80.1
Toluene	92.14	74.70	100	6.64E-03	0.05	110.6

Table 4
Continued

Candidate Compound	Molecular Weight	Vapour Pressure kPa	at Temp. (C)	Henry's Law Constant @ 25C (mta-m³/mole)	Solubility (g/100g)	Boiling Point (C)
Styrene	104.2	13.0	30		0.04	145.2
Ethyl Benzene	106.2	33.90	100	7.90E-03	0.01	136.2
Isopropyl Benzene	120.2	0.62	25	129E-03	0.005	154.2
Vinyl Chloride	62.5	3240.00	100	2.30E-02	0.25	-14
Methylene Chloride	84.93	600.00	100	3.39E-03	1.67	40
Ethylene Dischloride	98.96	14.00	30	5.32E-03	0.87	83.5
Chloroform	119.39	307.00	100	3.39E-03	0.93	61.2
Trichloroethylene	133.41	150.00	100	4.29E-03	0.11	74.1
Carbon Tetrachloride	153.83	200.00	100	2.13E-02	0.05	76.7
Perchloroethylene	165.83	6.00	40		0.015	121
Ethylene Dibronide	187.9	2.20	30	1.20E-03	0.431	131
Dichlorobezene	147.01	10.00	100	194E-03	0.015	180.5
Phenols	94.1	5.30	100		8.66	182
Cresols	108.1	0.66	76		2.4-3.1	191-202
Pentachlorophenol	266.4	0.03	100	1.40E-03	low	
Propylene Oxide	58.1	53.00	18		65	34
Vinyl Acetate	86.1	15.30	25		2.5	72
Carbon Disulphide	76.1	57.00	30		0.23	46.3
Turpentine	136+/-	0.66	25		low	154-170
Naphtha	varies	10.00	38		low	30-202
Tall Oil	varies				low	high

Process calculations for seven selected compounds were performed by RCC using an in-house program developed for its AquaDetox system. The results are presented in Table 5.

Table 5
PORTABLE COLUMN PERFORMANCE
ON SELECTED POLLUTANTS

Compound	Feed Flow (L/min)	Overhead (% of Feed)	Ratio (In/Out)	% Removal
1,1,1 Trichloroethane	26.5	20	11000	99.99
1,1,1 Trichloroethane	37.9	10	7300	99.99
1,1,1 Trichloroethane	121.1	1	1100	99.91
Benzene	26.5	20	10000	99.99
Benzene	37.9	10	6700	99.99
Benzene	121.1	1	1000	99.90
Ethylene Dichloride	26.5	20	11000	99.99
Ethylene Dichloride	37.9	10	6700	99.99
Ethylene Dichloride	121.1	31	530	99.81

Table 5
Continued

Compound	Feed Flow (L/min)	Overhead (% of Feed)	Ratio (In/Out)	% Removal
Methyl Ethyl Ketone	26.5	20	1100	99.91
Methyl Ethyl Ketone	37.9	10	476	99.79
Methyl Ethyl Ketone	121.1	1	20	95.0
(Reflux = 90%, all cases)				
2, Methyl, 1, Butanol	26.5	20	1000	99.90
2, Methyl, 1, Butanol	37.9	10	400	99.75
Methanol (Reflux = 0%)	30.3	20	143	99.3
Methanol (Reflux = 25%)	30.3	20	100	99.0
Methanol (Reflux = 50%)	30.3	20	63	98.4
Methanol (Reflux = 75%)	30.3	20	31	96.8
Pentachlorophenol	26.5	20	111	99.1
Pentachlorophenol	37.9	13	20	95.0

Notes:

1. All calculations are based on 6 metres of packing.
2. All compounds shown except methanol were assumed to have one-half their limiting solubility at 25°C as the feed concentration for these calculations.
3. The RATIO presented is the concentration in the feed divided by the concentration in the bottoms.
4. Reflux is based on percentage of overhead stream.

The most important conclusion from these results is that even for very low volatility compounds, such as pentachlorophenol, greater than 99 percent removal can be achieved. Compounds that are more volatile can be reduced in concentration by four or five orders of magnitude. There is a tradeoff in the case of water soluble compounds such as methanol. When the reflux ratio is increased, the removal efficiency decreases and the overhead concentration (not shown here) increases. The removal efficiency and overhead concentration can both be increased by reducing the feed rate.

All of these calculations are based on predictions of what the actual field conditions will be. It is useful, therefore, to examine the sensitivity of the process to a number of factors that cannot be controlled. The first major unknown is the influent concentration. In the case of low solubility compounds, all that is necessary is to provide the capability of phase separation in the feed tank to bring the influent concentration to a manageable level. For high solubility compounds, the remedy may not be so easy. Fortunately, it is basic to counter current mass transfer that the removal is logarithmic. A given increase in the feed concentration results in a much smaller increase in the effluent concentration. Increasing the steam to liquid ratio and decreasing the feed rate will improve the system performance.

It may happen that compounds other than those listed in Table 4 require emergency treatment. The computer model planned as a part of the system would provide accurate performance data, but in general any compound with one or more of the following characteristics could be considered for steam stripping:

- Vapour pressure higher than water
- Sparingly soluble in water
- High activity coefficient with respect to water

One other factor that may influence the system performance is the weather. In extremely hot temperatures, the heat rejection capacity of the condenser decreases and this may limit the overhead-to-feed ratio, the degree of subcooling possible, or the total feed rate, depending on the compound being stripped.

Implementation

A prototype unit capable of treating 2000 litres per hour should be built by next fall and ready for testing with contaminated groundwater.

RÉCUPÉRATION D'HYDROCARBURES LOURDS PAR INJECTION D'EAU À HAUTE TEMPÉRATURE; LESSIVAGE ET POMPAGE.

Alain Sauriol, géo. M.Sc.[1], Pierre Hudon, ing.[1] et John Primak, ing.[2]

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[2] Division CCR, Minéraux Noranda inc., Montréal-Est, Québec, Canada

Résumé

A l'arrière de l'usine d'électrolyse de la Division CCR, de la compagnie Minéraux Noranda inc., une aire d'approximativement 360 m^2 a été contaminée par de l'huile lourde. De façon générale, l'huile lourde se retrouvait dans le premier mètre du sol, plus précisément entre 30 et 90 cm de profondeur. L'excavation du sol contaminé étant exclue, une décontamination in-situ fut réalisée.

Au cours de l'été 1986, sur une période de 16 semaines, de l'eau à une température moyenne de 49°C fut injectée dans un puits. L'utilisation d'eau chaude assurait un meilleur nettoyage de l'horizon contaminé et servait d'indicateur pour connaître le cheminement de l'eau à l'intérieur du sol. Un puits de récupération, localisé à l'emplacement de la source du déversement, assurait le rabattement de la nappe phréatique et la récupération des hydrocarbures lourds provenant du lessivage du sol.

L'injection d'eau chaude, le rabattement de la nappe d'eau souterraine et l'écumage des huiles lourdes surnageantes ont permis de récupérer 2 320 litres d'hydrocarbures lourds.

Abstract

At the back of the electrolysis plant of the Division CCR of Minéraux Noranda inc. company, an area of approximately 360 m^2 has been contaminated with heavy fuel oil. Generally, the oil was found in the first meter of the soil, more precisely at a depth of 30 to 90 cm. Due to constraints related to plant operation, excavation of the contaminated soil having been excluded, an in-situ recovery of the oil was performed.

During the summer of 1986, over a period of 16 weeks, water at an average temperature of 49°C was injected in a well. The use of hot water, rather than water at ambiant temperature, provided a better cleaning of the contaminated area and served, with temperature measurements in observation wells, to confirm the groundwater flow pattern. A recovery well, located at the source of the spill, ensured the drawdown of the groundwater table and the recovery of the hydrocarbons.

The injection of hot water, the drawdown of the groundwater table and the skimming of the floating oil layer have led to the recovery of 2,320 liters of oil.

Introduction

Sise dans la municipalité de Montréal-Est, au coeur du complexe industriel de l'Est de l'île de Montréal, la Division CCR de la compagnie Minéraux Noranda inc., produit principalement du cuivre cathonique, de l'argent, de l'or et du sélénium.

Au cours de l'été 1985, des traces d'hydrocarbures lourds furent détectées dans un regard d'égout pluvial situé à l'arrière de l'usine d'électrolyse CCR. Afin de déterminer la source de contamination et d'évaluer l'étendue de la zone affectée, des travaux de caractérisation furent immédiatement entrepris.

Caractérisation

Tout d'abord, afin d'enrayer la migration des hydrocarbures dans le réseau d'égout pluvial, un ballon obturateur fut installé. Un couvercle étanche et une digue autour du regard (voir la figure 1) empêchèrent l'apport des eaux de ruissellement et évitèrent ainsi un éventuel débordement de l'égout.

Après examen des plans de l'usine, les hydrocarbures pouvaient provenir de deux sources. Les réservoirs de mazout ou une ancienne conduite d'alimentation souterraine reliant les réservoirs à une raffinerie voisine.

Douze tranchées d'explorations furent excavées et trois forages réalisés. Comme l'illustre la figure 1, des hydrocarbures furent notés tout le long de la conduite souterraine. Les sondages autour des réservoirs ne révélèrent aucune trace d'hydrocarbures.

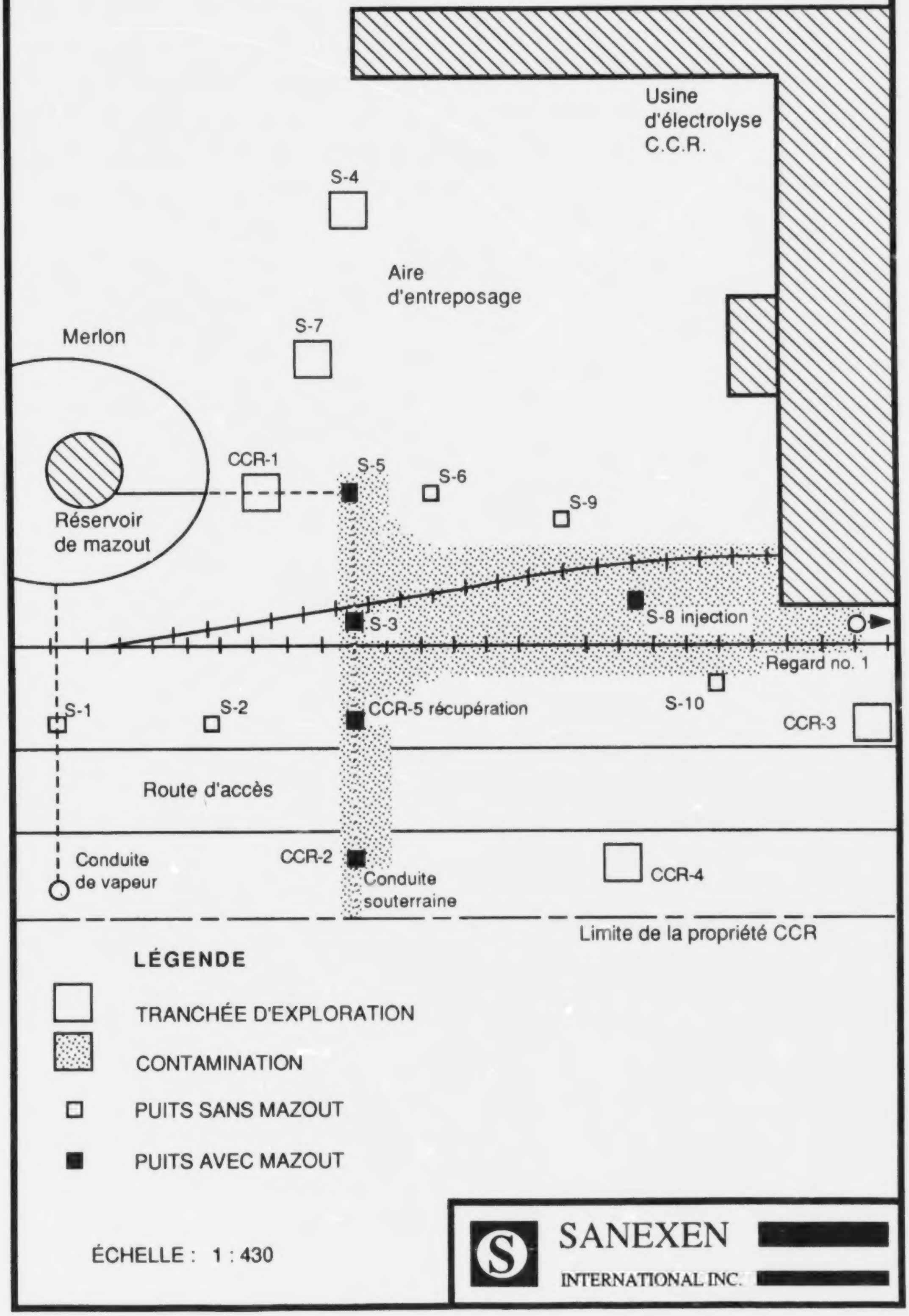
L'écoulement de la nappe phréatique se fait vers le Sud-Est, orientation générale dans cette partie de l'île de Montréal. Toutefois, un écoulement préférentiel à travers un horizon de sol perméable, sous la conduite ainsi que sous la voie ferrée, contrôle l'écoulement de l'huile lourde, vers le regard n°1.

De façon générale, l'huile lourde se retrouvait dans le premier mètre du sol, plus précisément entre 30 et 90 cm de profondeur. L'épaisseur du gravier contaminé était d'environ 60 cm. Une couche d'argile, sous le gravier, limitait la migration verticale de l'huile lourde. La superficie de la zone contaminée était d'environ 360 m^2. Une fois la source et l'étendue de la contamination connues, il fallait procéder à la restauration du site.

Restauration

La présence de deux voies de chemin de fer du Canadien National ainsi que la circulation lourde dans le secteur contaminé excluaient l'excavation du sol comme méthode de restauration. La solution retenue consistait à injecter de l'eau chaude dans l'horizon contaminé et à récupérer à l'aide d'un puits de récupération les hydrocarbures ainsi lessivés.

FIGURE 1. SUPERFICIE DE LA ZONE CONTAMINÉE ET LOCALISATION DES PUITS.


Usine
d'électrolyse
C.C.R.
S-4
Aire
d'entreposage
S-7
Merlon
CCR-1
S-5
S-6
S-9
Réservoir
de mazout
S-8 injection
S-3
Regard no. 1
S-10
S-1
S-2
CCR-5 récupération
CCR-3
Route d'accès
Conduite
de vapeur
CCR-2
Conduite
souterraine
CCR-4
Limite de la propriété CCR
LÉGENDE
TRANCHÉE D'EXPLORATION
CONTAMINATION
PUITS SANS MAZOUT
PUITS AVEC MAZOUT
ÉCHELLE : 1 : 430
SANEXEN
INTERNATIONAL INC.

Puits d'injection

Un puit d'injection fut installé à l'emplacement du puits d'observation S-8. D'une profondeur de 1,25 m, le puits reposait sur de l'argile. La figure 2 fournit une vue en coupe de l'installation. Lors de l'installation du puits on retrouva les hydrocarbures dans un horizon de gravier grossier entre 55 et 85 cm de la surface. Les horizons supérieurs ne montraient aucune trace d'huiles lourdes.

L'alimentation en eau était fournie 7 jours/semaine, 24 h/jour avec un débit moyen de 66 L/minute. L'injection d'eau s'étala sur une période de 69 jours.

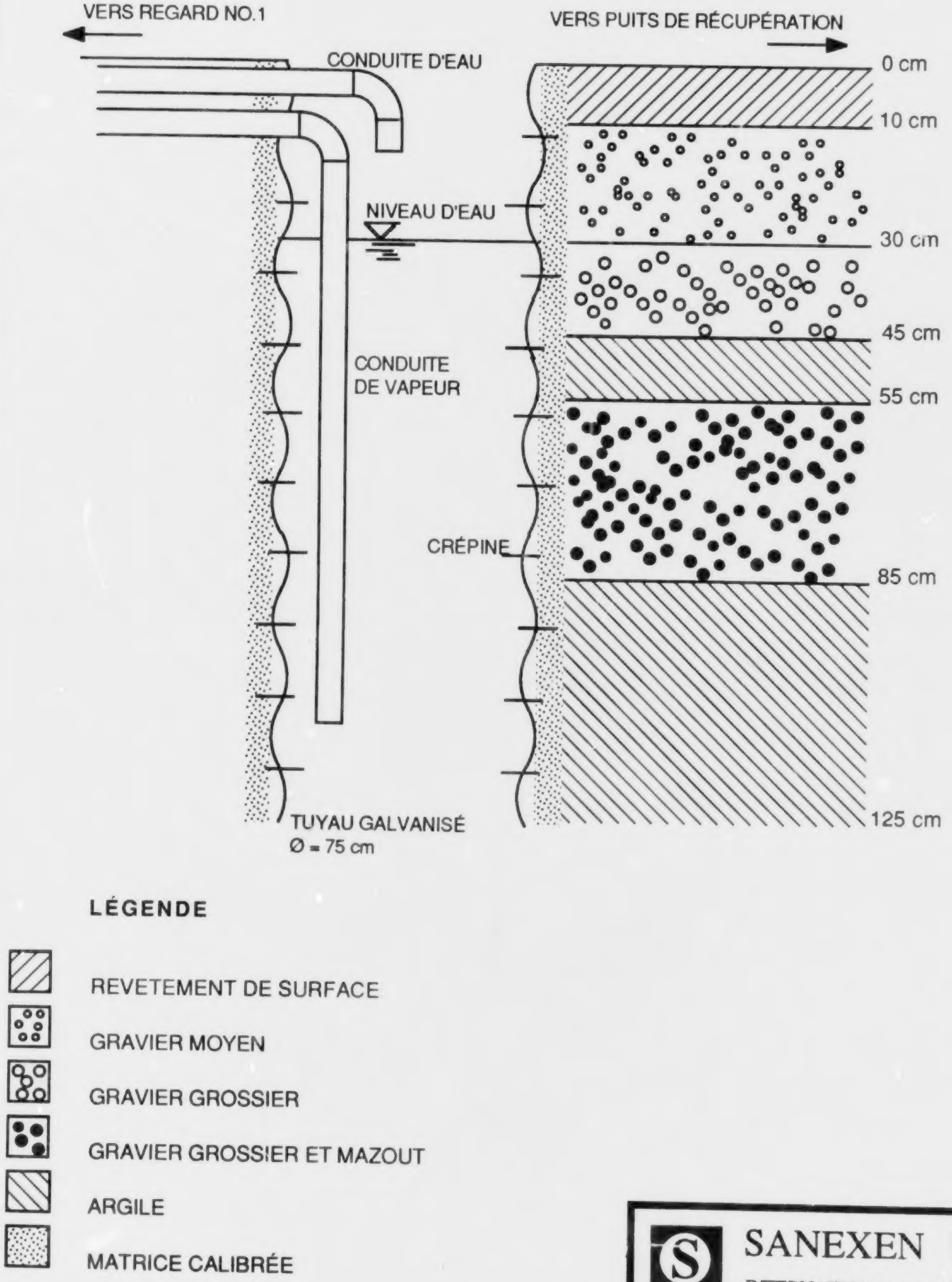
D'autre part, la température de l'eau à l'intérieur du puits était de 49°C en moyenne. L'utilisation d'eau chaude assurait un meilleur nettoyage de l'horizon contaminé et servait d'indicateur pour connaître le cheminement de l'eau à l'intérieur du sol. À cet effet, des mesures bimensuelles de température de l'eau furent prises à l'intérieur de différents puits d'observation. Ces mesures indiquent clairement que l'eau injectée cheminait suivant un écoulement préférentiel, inverse à celui utilisé par l'huile lourde. De plus, des échantillons d'eau furent prélevés dans les puits S-6, S-9, S-10 afin de s'assurer qu'aucune huile ne chemine au delà de la zone contaminée.

Puits de récupération

Le puits de récupération permettait l'abaissement du niveau d'eau et par voie de conséquence, le captage de l'huile libre dans le sol. Pour réaliser ce double objectif, un puits à double tubage fut installé. Le premier tubage, formé d'un tuyau galvanisé de 75 cm de diamètre, était perforé sur toute sa longueur. Un second tubage, non perforé, de 25 cm de diamètre, servait à isoler la pompe submersible des hydrocarbures qui s'accumulaient dans le premier tubage. Ainsi, il était possible de pomper et d'abaisser la nappe tout en conservant l'huile à l'intérieur du puits. Ce système avait l'avantage d'être simple et de ne nécessiter qu'une surveillance minime (voir la figure 3).

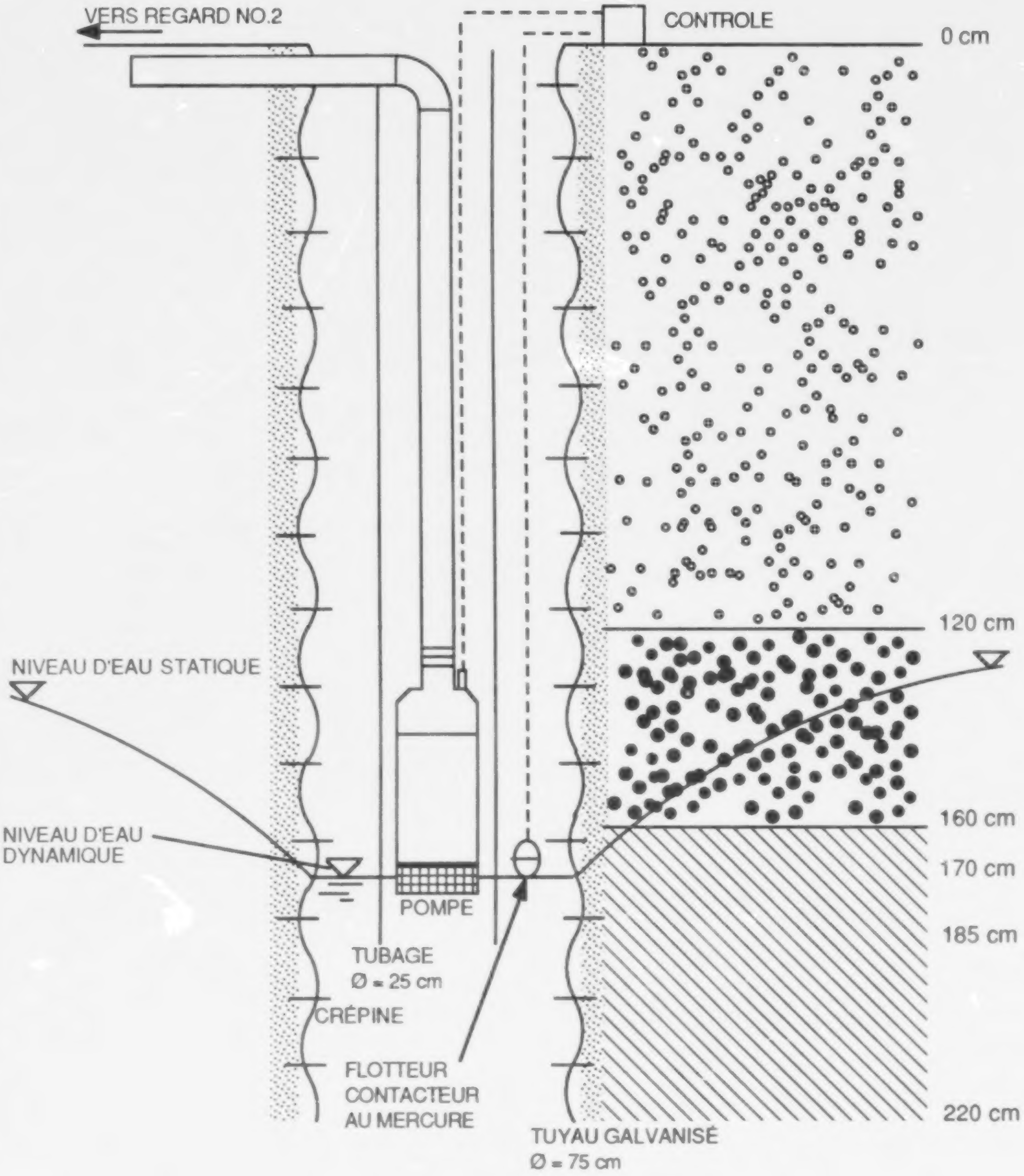
Le puits fut localisé à l'emplacement du puits d'observation CCR-5. La pompe submersible, reliée à un flotteur avec contacteur au mercure avait une fréquence moyenne de pompage de 18 fois par heure pour un débit d'eau moyen horaire de 3 000 L/heure.

FIGURE 2. VUE EN COUPE DU PUITS D'INJECTION.


VERS REGARD NO.1
VERS PUITS DE RÉCUPÉRATION
CONDUITE D'EAU
NIVEAU D'EAU
CONDUITE DE VAPEUR
CRÉPINE
TUYAU GALVANISÉ
Ø = 75 cm
0 cm
10 cm
30 cm
45 cm
55 cm
85 cm
125 cm
LÉGENDE
REVETEMENT DE SURFACE
GRAVIER MOYEN
GRAVIER GROSSIER
GRAVIER GROSSIER ET MAZOUT
ARGILE
MATRICE CALIBRÉE

SANEXEN
INTERNATIONAL INC.

FIGURE 3. VUE EN COUPE DU PUITS DE RÉCUPÉRATION.


VERS REGARD NO.2
CONTROLE
0 cm
120 cm
160 cm
170 cm
185 cm
220 cm
NIVEAU D'EAU STATIQUE
NIVEAU D'EAU DYNAMIQUE
POMPE
TUBAGE
Ø = 25 cm
CRÉPINE
FLOTTEUR CONTACTEUR AU MERCURE
TUYAU GALVANISÉ
Ø = 75 cm

LÉGENDE

- ⁘ GRAVIER MOYEN
- ● GRAVIER GROSSIER ET MAZOUT
- ▨ ARGILE
- ░ MATRICE CALIBRÉE

SANEXEN
INTERNATIONAL INC.

Lors des opérations d'écumage des huiles surnageantes, on récupérait en moyenne 70 litres d'hydrocarbures par visite. Au total, environ 2 270 litres d'huiles lourdes furent récupérés. La reprise des travaux à l'été de 1987 n'a permis de récupérer qu'environ 50 litres d'huiles lourdes sur une période de 6 semaines. Lors des dernières visites les quantités d'hydrocarbures étaient très faibles.

Par ailleurs, des échantillons de l'eau pompée, à partir du puits de récupération, furent régulièrement prélevés afin de vérifier le non dépassement de la norme de rejet de 30 mg/litre pour les huiles et graisses, norme établie par la Communauté Urbaine de Montréal. Les résultats d'analyses démontrent que les échantillons d'eau ne dépassèrent pas la norme de 30 mg/litre.

Conclusion

L'injection d'eau chaude, le rabattement de la nappe phréatique et l'écumage des huiles surnageantes ont permis de récupérer 2 320 litres d'hydrocarbures. À la fin des travaux, aucune pellicule d'huile n'était notée dans le regard n°1. De plus, les quantités d'huiles lourdes récupérées dans le puits de récupération étaient réduites presque à zéro.

L'utilisation de cette technique à permis de récupérer l'ensemble des huiles mobilisables et d'enrayer la migration des hydrocarbures dans le sol. Les huiles résiduelles (non mobilisables) seront lentement biodégradées par la flore microbienne du sol.

Dans un contexte de production industrielle, cette technique avait l'avantage de n'interférer en rien avec les opérations normales de l'usine. En aucun temps, la circulation ferroviaire et routière ne fut interrompue en raison des travaux de décontamination en cours.

Finalement, l'ensemble de l'opération s'est faite en maintenant informé la Direction régionale de Montréal du Ministère de l'Environnement du Québec et le Service de protection de l'Environnement de la Communauté Urbaine de Montréal.

Les travaux furent définitivement interrompus le 23 juillet 1987.

Development and Testing of a Mobile Micro/Ultrafiltration Unit

Diane Radnoff, Edward Middleton, Harry Whittaker

Introduction

The Environmental Emergencies Technology Division (EETD) of Environment Canada has had much experience in the development and use of Reverse Osmosis (RO) in landfill and spill clean-up. However, under field conditions, the raw effluent tends to contain a large amount of particulate and/or oily materials. These can often clog or damage a RO membrane if they are not removed. To this end, EETD designed and built a Mobile Micro/Ultrafiltration Unit in conjunction with Seprotech Systems Incorporated.

Microfiltration (MF) is a physical separation procedure that involves the filtration of particles in the size range of 0.1 to 10 microns. Because membrane/solution/ solute interactions are generally not involved in these techniques, it is usually easy to estimate the performance of the filter on the waste given that information is known on the composition of the liquid being filtered. Moreover, these methods require a low (often less than 100 psi) operating pressure which represents a saving in power consumption costs.

The advent of tubular MF and UF membranes has further simplified the process. A tubular membrane can treat slurries of even a toothpaste-like consistency without plugging. (The system will be limited by the capabilites of the feed pump being used.) In addition, since many of these membranes can be relatively easily cleaned, they can be re-used.

Background

The design of the MF/UF system for Environment Canada was accomplished through the combination of specifications supplied by Environment Canada and the knowledge and expertise of Seprotech Systems Incorporated.

Of major concern throughout the design was the need to supply a system that would meet all the required specifications and remain within the budget constraints of the contract. Being familiar with the testing procedures and wide variability of the tests and treatment processes that are performed by EETD, Seprotech designed the system to allow for as many changes and operating conditions as possible. The unit is illustrated in figures 1 and 2.

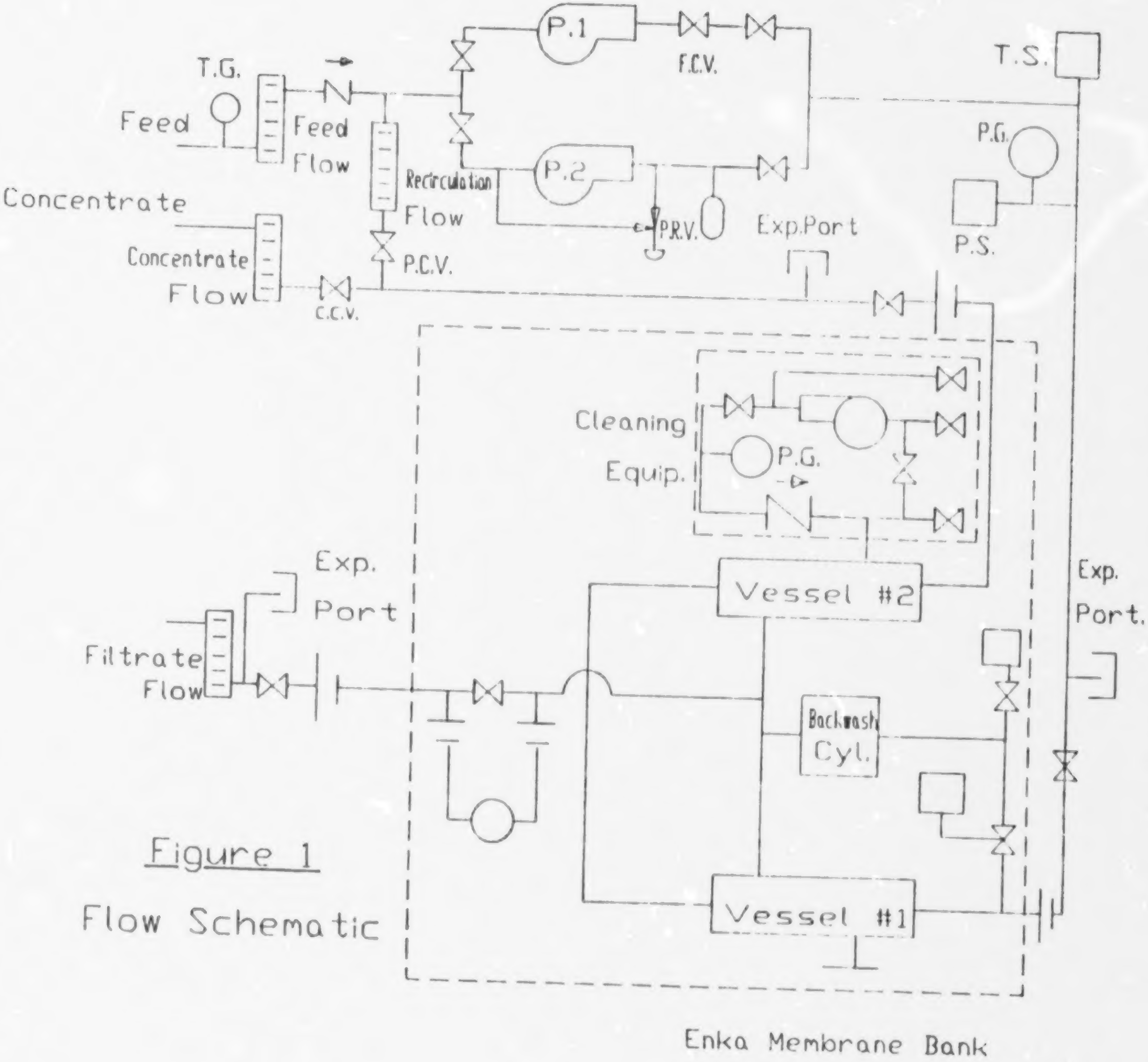

T.G.
Feed
Feed
Flow
Recirculation
Flow
P.C.V.
Concentrate
Concentrate
Flow
C.C.V.
P.1
P.2
F.C.V.
P.R.V.
Exp.Port
T.S.
P.G.
P.S.
Cleaning
Equip.
P.G.
Exp.
Port
Filtrate
Flow
Vessel #2
Backwash
Cyl.
Vessel #1
Exp.
Port.
Enka Membrane Bank

Figure 1

Flow Schematic

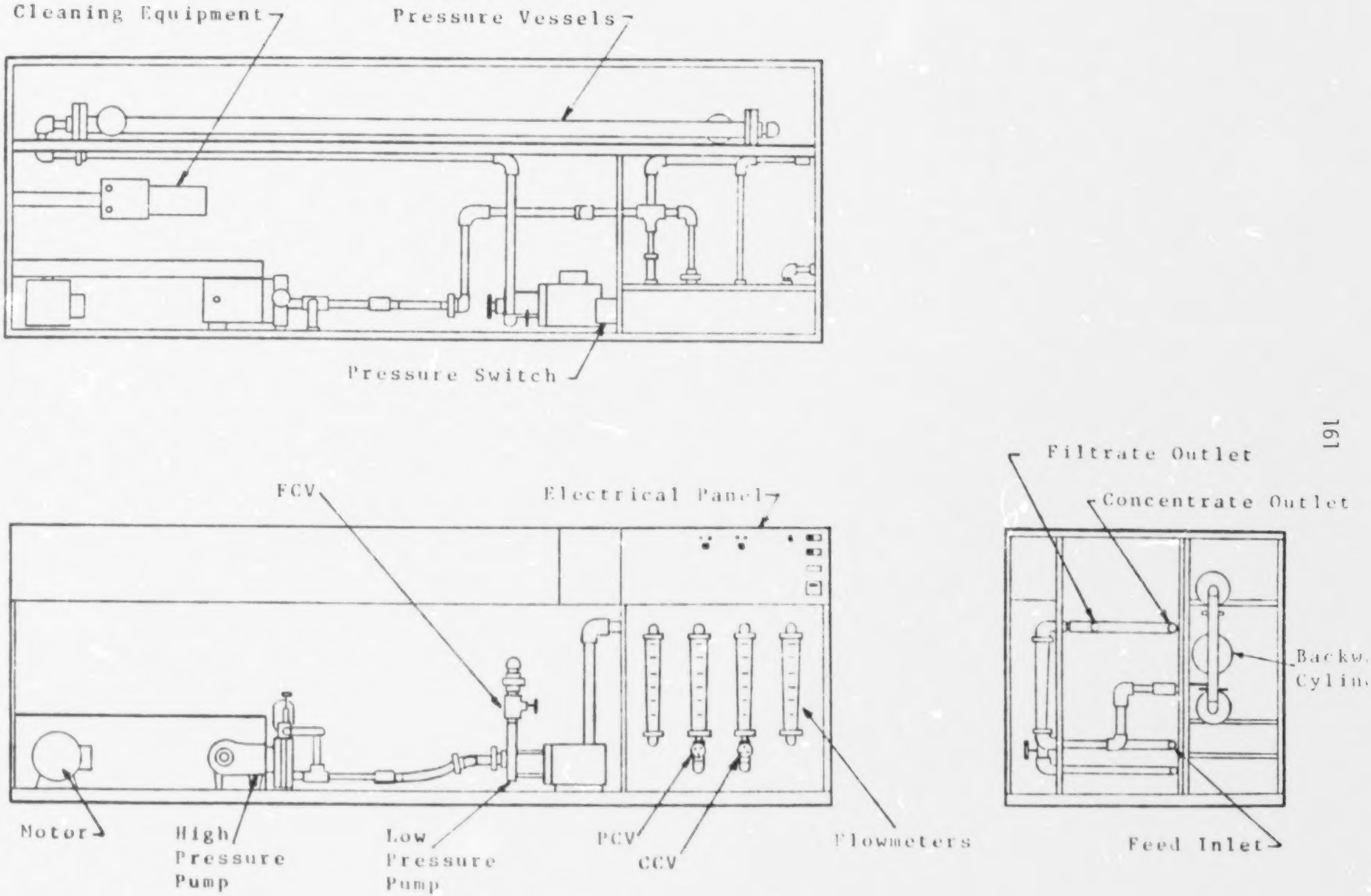

Cleaning Equipment
Pressure Vessels
Pressure Switch
FCV
Electrical Panel
Motor
High Pressure Pump
Low Pressure Pump
PCV
CCV
Flowmeters
Filtrate Outlet
Concentrate Outlet
Backw.
Cylin.
Feed Inlet

Figure 2 System Layout

Design Specifications and Solutions

1) **Size** The maximum size was not to exceed 3.0 meters by 1.2 meters by 1.2 meters and the maximum weight was not to exceed 500 kilograms. To allow for greater variability in use, the frame dimensions were set at the maximum allowable size. This left space for the expansion of the unit to contain special equipment and/or additional membrane banks for specific application tailoring.

2) **Capacity** The filtrate capacity of the unit was required be at least 40 litres per minute (L/min) at a feed solution of no more than 1000 ppm of oil and grease. To satisfy this and to be compatible with the operating chemicals as mentioned in section 5 to follow, the choice of the Enka MF element was made. The membrane, membrane housing and membrane sealants are all polypropylene leaving little concern for the compatibility of the feed and membrane. The unique backwash ability of the membrane allows for longer running time between washes and higher filtrate fluxes than conventional MF elements.

3) **Pressure Range** The unit had to be capable of operating at a controlled pressure of between 175 and 1350 kPa (25 and 200 psi). To keep the power consumption and costs to a minimum, the use of two pumps was chosen. A stainless steel centrifugal pump was selected and sized to supply enough feed flow for the Enka membranes or for up to two other MF or UF membranes run in parallel. This pump can supply feed for low pressure applications up to 45 psi. For high pressure applications between 45 and 200 psi, a Magikist piston pump was chosen. This pump will allow for configurations up to and including four inch MF/UF elements in series. The Magikist pump is made of bronze and has been used by EETD extensively. It tends to hold up well under adverse conditions and the cost of such a pump allows for its replacement numerous times over before the benefits of a much more expensive pump outweigh its use. The Magikist was also chosen so that a bank of RO membranes could be run at 500 psi if so desired. This would negate the need to have to transport two separate units to a test site.

4) **Recycle** The unit was equipped with valving and a gauge to enable a controlled amount of the concentrate to be recycled for further concentration.

5) **Materials of Construction** The materials used had to be compatible with concentrated solutions of inorganic chemicals (up to 35% sodium chloride) and weaker solutions of halogenated organic chemicals (up to 10% ethylene dichloride). In addition, chemical solutions

in the range of pH 2 to 12 could be encountered. To prevent corrosion of the plumbing, polypropylene and stainless steel were used extensively throughout. All piping not required to withstand 45 psi was plumbed polypropylene and the remainder was plumbed stainless steel. Flowmeter material was chosen to be polysulphone as visual flowmeters were specified to keep costs down.

Other Design Features

Transportability: The unit was designed so as to allow for movement by a forklift or overhead crane.

Expandability: The plumbing and frame design allow for an additional bank of membranes to be hooked up. Once the additional bank is in place, switching from one bank to the other is made easy through simple valve closures/openings.

Versatility: The plumbing configuration was designed for easy change from one bank to another as well as from low pressure to high pressure operation. Additional space in the unit also allows for easy modification for specific applications.

Controls: The majority of the controls were centrally located to shorten operational procedures and lessen operator fatigue. To allow for unmanned operation and shutdown, automatic controls for low feed rates, plugged membrane elements and excessive temperatures and pressures were added. The system also comes with a fully adjustable backwash cycle and backwash duration control system.

The Enka Membrane

The membrane utilized with the MF unit was the Enka Microdyne® Module (model MD 080 TP 2L) as shown in figure 3. As mentioned before, the membrane, the housing and the potting are all constructed of polypropylene. The module contains 43 tubes with an inner diameter of 5.5 mm and pore size of 0.2 microns. The operating pressure is 40 psi and the membrane can withstand temperatures of up to 60 degree celsius.

The module has been designed for crossflow MF applications; that is, the separation of suspended solids down to particles of 0.2 microns and for emulsions of low concentration. Although two filtrate outlets are present, normally only one is used. If the module is installed in a horizontal position, the outlet at the low pressure side of the membrane is employed.

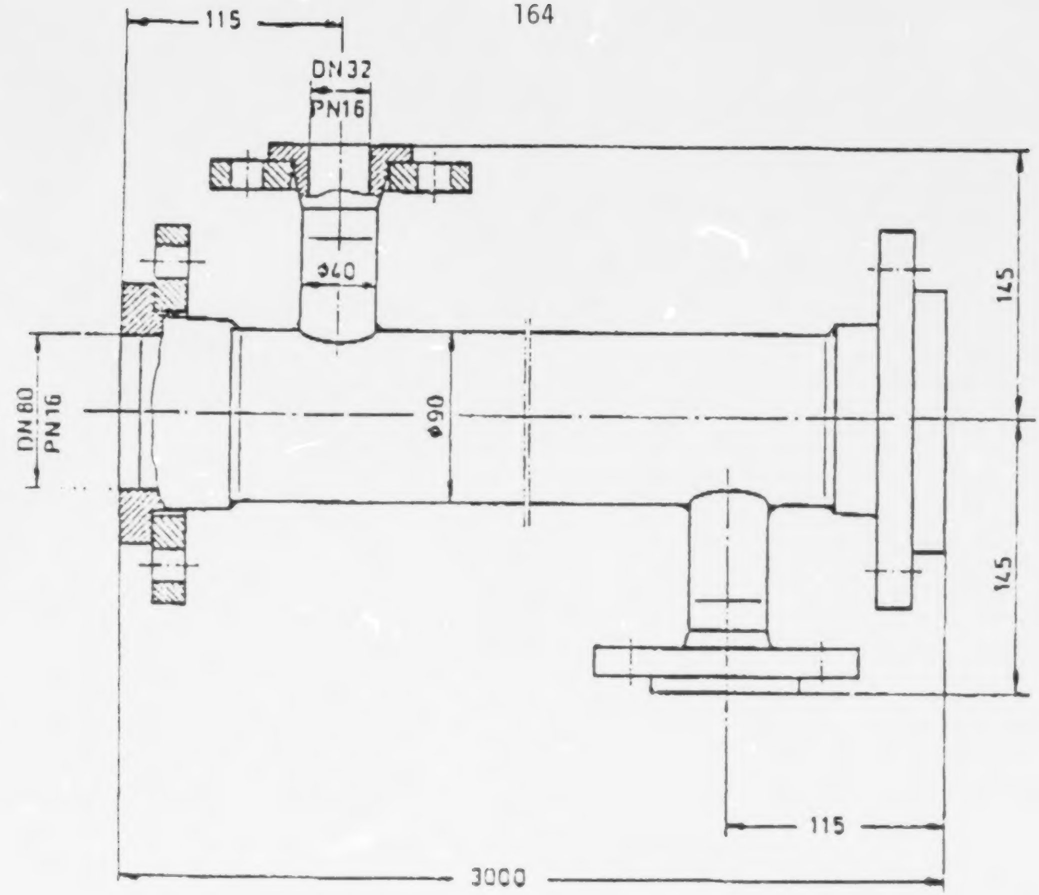


Figure 3: The Enka MF Membrane Module

Due to its material of construction, the membrane has good resistance to many organic and inorganic substances, but is hydrophobic by nature. This means that liquids such as water with a high surface tension of 0.072 N/m do not wet the membrane. Therefore, for filtration of slurries from water, the membrane has to be activated by means of water soluble liquids with surface tensions less than 0.035 N/m. The following liquids may be used:

- ethanol
- isopropanol
- a solution of water and 40% by vol. isopropanol
- a solution of water and 25% by vol. tert. butanol (this solution is flammable)
- 5% aqueous solution of Lutensite A-LBA resp. AES (a product made by BASF)
- a surfactant (for pre-wetting on a long term basis)

Liquids containing a large amount of gases (for example, carbonated beverages or beer) require a counter pressure on the filtrate side of the membrane in order to prevent the release of gases. Otherwise, these gases will cause the membrane to lose its conditioning and become hydrophobic again. The membrane may also be drained and stored dry. (This is desirable when freezing temperatures are likely to be encountered during storage of the membrane.)

The Test Solution

In the past, EETD has treated pesticide-contaminated water with RO. However, as this waste typically contains a high particulate loading, RO membranes quickly become fouled. Not only would MF be useful here as a pre-treatment step for RO, but if powdered activated carbon (PAC) were added to the waste prior to treatment by MF, possibly a large amount of the contaminants could be removed as well.

The test solution was a sample of pesticide contaminated water with a Total Organic Carbon (TOC) content of approximately 1500 ppm. Although it contained more than fifty different types of pesticides, the following were found in the highest concentrations:

Triallates
Bromoxynil
2,4-D
MCPA
Diclofop methyl
Trifluralin
Dicamba

The above chemicals represent 80%[1] of the pesticides used, by volume, in Western Canada. Thus, this treatment method may also show promise as a means of handling the large volumes of pesticide-contaminated water that arise each year as a result of the pesticide can triple rinsing program.

Since little was known of the slurry handling capabilities of the MF unit, it was decided to try two different PAC loadings; 1 and 2 g/L. Future testing could further examine the equipment's limitations as well as the optimization of carbon addition. The carbon was added to the waste and the mixture was stirred for three hours to allow the contaminants to adsorb.

Preliminary Testing

Preliminary experimental work was done on the test solution with an Enka MD 020 TP 2N module. This membrane module contains 3 tubes with an inner diameter of 5.5 mm and pore size of 0.2 microns. Since it is only 1 metre in length (as compared to the MD 080 TP 2L module which is 3 metres long) it has approximately 1/111 the area of the larger module. The preliminary testing was carried out to determine the membrane compatibility with the pesticide contaminated water as well as the efficiency of this method as a means of removing the pesticides. The testing would also determine the optimal filtrate flowrates and the amount of time the system could run before the membranes had to be cleaned. If the flowrates were too low or the time between cleanings was too short, it would indicate that this particular membrane would not be suitable for this application. The test system is shown in figure 4.

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[1] Miles Constable, Restricted Business Information--Trend and Use Pattern Analysis for Regional Priority Pesticides, Western and Northern Region, Conservation and Protection, Environment Canada, Dec 1986, pg. 7.

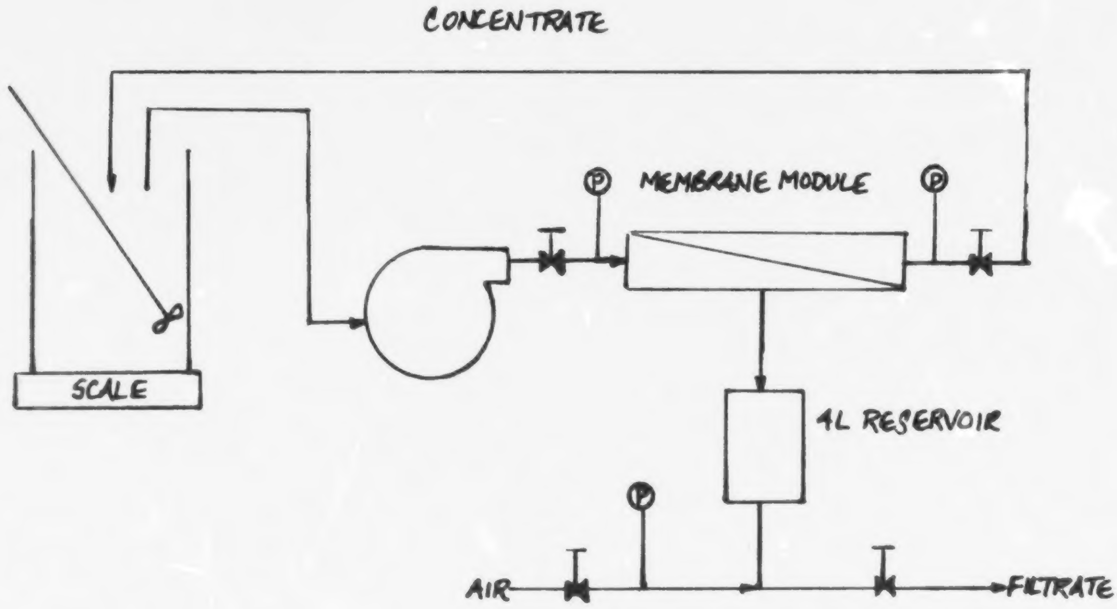


Figure 4: Preliminary Testing System

The membrane was pre-treated with isopropanol and then water base line testing was done to determine the maximum flowrates attainable from the module. Unfortunately, the filtrate fluxes were very low. The membrane manufacturer specified that this module would give 1 L/min while in reality the filtrate flowrates declined from approximately 1 L/min to a steady state rate of 100 mL/min. As the water used was pre-treated by RO, this decline cannot be attributed to fouling in the normal sense (that is, inorganic fouling or bacterial growth) and must have resulted from the damage of the membrane by this water. (In fact, electron microscope pictures taken of the membranes bore this out.) However, testing was still carried out, with the backwash system dismantled (due to the large amount of time it took to fill the 4 L reservoir), to determine how well the pollutants could be removed by this process.

The runs were as follows:

1) Operation for two hours to determine the steady-state filtrate flux.
2) Operation for six hours to determine the long term behaviour of the membrane.
3) Operation with a concentrated feed solution. (The volume of the solution was reduced by one third.)

After each run, samples of the filtrate were taken and analyzed by GC/MS. These results are listed in Table 1.

It was apparent that the removal of the pesticides was dependant on how well they adsorbed on the PAC or adhered to particulate present in the solution. This was necessary as the membrane pore size only allowed for the removal of the carbon and other particulates. Thus, those pesticides that adsorbed well or adhered to particulate were removed well. This indicates that this method, by itself, is insufficient to completely treat this type of waste as many pesticides do not adsorb on carbon, but would produce a filtrate of high enough quality to be fed to RO without the problem of membrane fouling. Indeed, the filtrate was clear with no indication of suspended solids. In spite of the fact that few backwashes were accomplished during the testing, the filtrate flowrates declined very slowly, such that membrane cleaning was only necessary at the end of each run. Although, the filtrate flowrates were low (due to the damage sustained by the membrane), it was felt that, based on the results from the preliminary testing, it would be feasible to utilize this membrane as part of a treatment process for pesticide-contaminated water.

Pesticide	Feed no PAC (ppb)	*Feed (ppb)	Conc Feed (ppb)	*Filtrate (run 1) (ppb)	*Filtrate (run 2) (ppb)	Filtrate (run 3) (ppb)
Dicamba	1147	5	957	5	5	1147
MCPA	6576	200	6058	200	200	4768
2,4-D	7000	48.5	7094	20.2	LDL	6305
Trifluralin	6873	----	1530	----	----	0.15
Triallates	8764	77.0	2792	1.02	0.44	0.60
Diclofop	805	----	450	----	----	ND
Bromoxynil	2040	----	1903	----	----	1112

Table 1: Results from GC/MS Analysis of Samples

Note: Two laboratories conducted the analysis, Envirotest and Canviro (those marked with an asterisk). The difference in the results can be attributed to the use of different solvents to extract the pesticides for analysis. Envirotest used diethyl ether, Canviro used hexane. The effect of the use of different solvents can be seen in the article by Cessna, et al; ("A

Multiresidue Method for the Analysis and Verification of Several Herbicides in Water",Journal of Agriculture and Food Chemistry, 1985, vol 33, pp 504-507).

Water Base Line Test With the MF/UF Unit

Water base line testing was conducted prior to the trials with the MF unit. At a feed flowrate of 150 L/min (40 USgal/min) and a pressure of 45 psi, the membranes produced 900 L/hr of filtrate. The membranes had, during an earlier test, produced 2400 L/hr of filtrate. However, during the first test, the filtrate:concentrate ratio was controlled to 4:1. Although this caused the filtrate flowrates to increase, it also caused the flow across the membrane to reduce. This is not a problem where only water is being used, but with a waste solution containing suspended solids the membrane will foul very quickly if the flow across it is insufficient to "scour" away particulate before it can adhere to the membrane.

Test Procedure for the MF/UF Unit

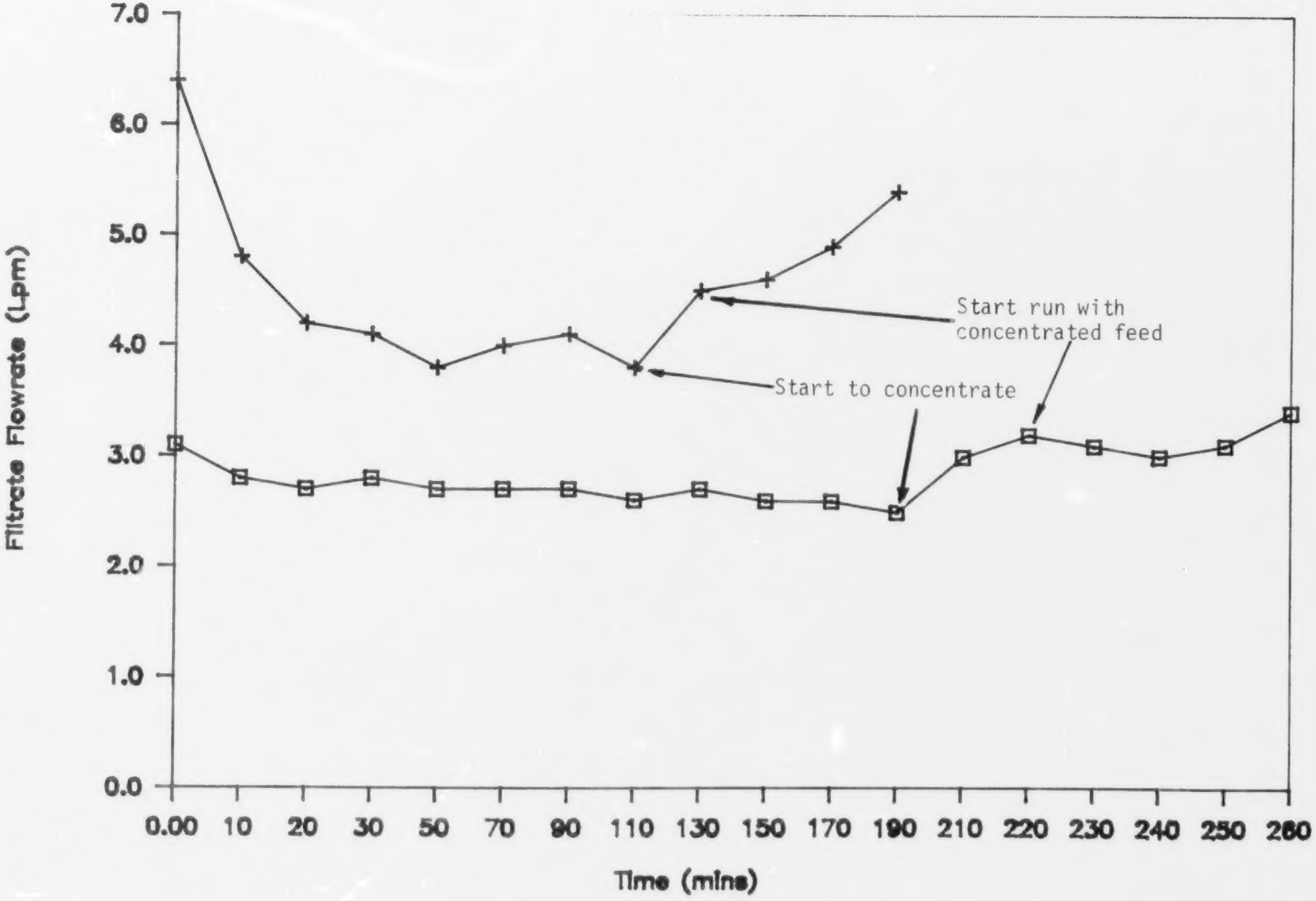
Approximately 200 litres of pesticide contaminated wastewater was mixed with 1 g/L of PAC (65% through a 325 mesh) and was stirred for three hours for the first set of trials. As the pH of the solution was 10, Hydrochloric Acid was added to reduce the pH to 4.5 and thus prevent calcium carbonate scaling. A PAC loading of 2 g/L was used for the second set of runs. The unit was then operated for at least 2 hours on this solution at a feed rate of 140 L/min (37 USgal/min) and a pressure of 45 psi. Samples of the feed and filtrate were taken after two hours. The feed solution was then concentrated by 100% by reducing the volume by one half. The unit was run on the concentrated solution for one hour, at the end of which samples were taken as before.

Flowrates and pressure readings were taken at 20 minute intervals for the first run and every 15 minutes for the concentrate run. In addition, the unit automatic backwash system was set to backwash the membranes every 5 minutes.

Test Results

The plot of filtrate flowrate over time is shown in figure 5. From past experience with MF, it was estimated that the filtrate flowrates during the PAC trials would be approximately one fifth of those achieved during the Water Base Line testing. In fact, the membranes achieved rates, for the most part, that were higher than this. That is, a maximum filtrate flowrate of 400 L/min was attained in the 2 g/L runs. For both PAC loadings, the flowrate reached a steady state value and remained constant at that value over time. However, when the feed solutions were concentrated, the flowrates increased. This can be attributed to the scouring

Figure 5: Filtrate Flowrates over Time



action by the PAC. As long as the feed flowrate was maintained at approximately 150 L/min (40 USgal/min), the passage of the PAC past the membrane surface would tend to scour any particulate that may have been deposited there thus reducing the tendency for the membranes to foul. Eventually, as the feed becomes more concentrated, the capacity of the system to handle the slurry will be reduced and fouling will occur because the feed flowrate cannot be maintained. Obviously, the solids handling capacity of the membranes had not even been reached with the concentrated 2 g/L PAC solution as seen by the increase in flowrates with this solution.

The ability of this process to remove contaminants had been examined in the preliminary testing. Those contaminants that adsorbed well or adhered to suspended solids were removed well. However, there was a visible improvement in the quality of the filtrate that had been produced during the run with a PAC loading of 2 g/L. The filtrate that was generated during the 1 g/L trial was clear but has a yellow colour. This colouration was almost gone with the higher PAC loading. In addition, the filtrate from the first trial tended to foam much more and had an obvious odour of pesticides.

In order to determine the efficiency of the membranes to remove suspended solids, samples were taken during the runs. The liquid was evaporated and the residue in each case was weighed. The results of this test are given in table 2. Again, the quality of the filtrate improved as the concentration of the PAC increased.

Sample	Amount of Residue (g/100mL)	Efficiency of Run (% removal of particulate)
Raw Feed	0.14	
PAC + Feed (1 g/L trial)	0.30	
Filtrate	0.20	33.3
Conc PAC + Feed (1 g/L trial)	0.51	
Filtrate	0.02	96.1
PAC + Feed (2 g/L trial)	0.36	
Filtrate	0.09	75.0
Conc PAC + Feed (2 g/L trial)	0.63	
Filtrate	0.10	84.1

Table 2: Residue Analysis

Future Work

Following the residue analysis, some of the filtrate was passed over Granular Activated Carbon (GAC) of size 20 by 50 mesh. The effuent from the column was clear and colourless and had almost no odour. From this, it can be seen that GAC may be more suitable for this type of treatment in order to maximize the removal of contaminants. EETD plans to investigate this with MF membranes that have a tube diameter of 12 mm (half an inch) and pore size of 0.2 microns. The Enka membranes presently in the unit have a tube diameter of 5.5 mm (one quarter inch) and would probably become plugged too quickly if GAC were used.

The system will be refitted to hold UF membranes in order to determine their ability to treat contaminated waste. Since the unit has enough space to hold at least two more banks of membranes, many different membranes can be used and tested. This will be an ongoing project at EETD.

Finally, the system particulate handling capacities will be examined. This will not only be dependant on the types of membranes that are being utilized but also on ability of the pump to handle slurries. This will be a useful tool where the unit is to be used on a treatment and the volume of the waste must be reduced to a minimum.

References

Allan J. Cessna, Raj Grover, Lorne A. Kerr and Melonee L. Aldred, "A Multiresidue Method for the Analysis and Verification of Several Herbicides in Water", Journal of Agriculture and Food Chemistry, 1985, vol. 33., pp. 504-507.

Miles Constable, Restricted Business Information--Trend and Use Pattern Analysis for Regional Priority Pesticides, Western and Northern Region, Conservation and Protection, Environment Canada, Dec 1986.

Development and Demonstration of a Mobile Membrane and Adsorption System for Spill Cleanups: Ultrafiltration and System Costs

H. Donison and S. McDougall, ZENON Environmental Inc.

Abstract

Ultrafiltration as a pretreatment process for a mobile reverse osmosis (RO)/carbon adsorption treatment system was investigated and demonstrated. Without pretreatment, suspended solids and oil and grease fouled the RO membranes and caused operational problems. Ultrafiltration was shown to effectively remove suspended solids and oil and grease and is resistent to fouling. The quality of the final effluent achieved with UF pretreatment was superior to that achieved without pretreatment.

Based on the experience accummulated during two 60 day demonstration trials and a five day trial of ultrafiltration, a portable environmental clean-up system was designed and costed. The system incorporates reverse osmosis and carbon adsorption with optional ultrafiltration pretreatment. The capital cost of the complete system producing 36,000 L/day of treated effluent would be $130,000 while the operating and maintenance cost would be $265/day of operation.

Background

In the spring of 1986 a study was undertaken by ZENON Environmental for the Environmental Emergencies Technology Division (EETD) of the Environmental Protection Service to develop and demonstrate a mobile reverse osmosis/adsorption system for treating water contaminated by organic chemicals. The system was to be suitable for use by both government and industry for the long-term cleanup of large plumes of organically contaminated groundwater as well as the relatively short term cleanup of organic chemical or petroleum product spill sites.

A schematic of the fundamental system configuration is shown in Figure 1. The treatment system consisted of two primary unit operations. The organically contaminated water is processed by reverse osmosis to produce a clean stream for discharge and a stream for further processing in which the organic contaminants have been concentrated up to ten times the original concentration. The concentrated stream is treated in granular adsorbent columns where the organic contaminants are removed and an effluent suitable for discharge produced. The ultimate result of treatment is that the contaminated water can be treated on-site to produce a dischargeable effluent and the organic contaminants can be removed from the site adsorbed on a relatively small amount of carbon for incineration or disposal at a secure landfill.

For the purposes of this project, the EETD supplied their mobile reverse osmosis unit. This system can contain up to 12 spiral wound membrane modules in six pressure vessels. The other major unit was a skid mounted, column adsorption unit. This unit with its associated prefilter, was supplied by the Wastewater Technology Center, Environment Canada.

For development and demonstration of the RO/adsorption system, two contaminated water sources were chosen for treatment. One source was the contaminated leachate from the Gloucester Landfill, a former chemical waste landfill. This site was chosen as an example of the type of site that would require cleanup of large plumes of contaminated groundwater. The other source chosen for demonstration treatment was drainage water from a petroleum and petrochemical transfer station. This site reflected the kind of water that would be encountered in the cleanup of surface and runoff water contained after a spill or other accidental release of organic chemicals. The system was demonstrated for 60 days at each of the two contaminated sites. The results of these demonstrations are reported in an earlier paper on this study (Donison et.al. 1987)

These demonstrations showed that reverse osmosis technology can be used to successfully treat water contaminated by toxic volatile organics and that granular activated carbon adsorption columns can be successfully used to remove the toxic volatile organics from the concentrate produced by RO processing. However, the study also showed that the presence of significant quantities of suspended materials or iron cause operational problems which limit the success of RO processing under these conditions. When these conditions exist at a spill site, more extensive pretreatment than simple prefiltration is required.

During the demonstration at the petroleum and petrochemical transfer station considerable operational problems were caused by suspended solids, oils and grease and iron. Thus a further trial was conducted which included pretreatment of the RO feed by ultrafiltration (UF).

Ultrafiltration Pretreatment Trial

Figure 2 shows the unit processes and the process streams for the system used in this trial.

The UF system consisted of a feed and a wash tank, a heat exchanger and 2 banks of membranes in parallel each containing 6 pressure vessels. Each pressure vessel contained 3 tubular membranes. Due to limitations in the electrical supply only one bank was used during this trial. A schematic of the UF system is shown in Figure 3. The membranes used for this trial were ZENON BSC blend membranes. These polysulphone based membranes are hydrophilic membranes with good chemical resistence. These membranes have been used successfully in the past for the separation of suspended oil from water. The membranes were expected to provide a permeate flux rate of $2m^3/m^2$/day (50GFD) at 50°C and 205 KPa (30 psi) based on use for the treatment of other oily wastewaters.

The UF unit was operated in a batch mode, the concentrate from the membranes recirculated back to the feed tank and the permeate sent to the RO feed tank as shown in Figure 3. The feed tank was filled to the 640L level with drainage water contaminated with petroleum products. Each run could produce 440L of UF permeate (RO feed) as the capacity of the UF system was 60L and the pump on the UF unit shut off automatically when the level in the feed tank was 140L. To produce a final concentrate of 90% concentration of feed 2000L of feed needed to be processed, requiring 4.5 runs (440L of UF permeate produced after each run).

The final concentrate was emptied into a drum and the solids allowed to settle and the oil float to the top for a period of at least 24 hours. The clarified middle portion was added to the feed of a subsequent batch process. In this way the amount of concentrate produced requiring further treatment could be minimized.

The inlet pressure of the feed entering the membranes was about 384 KPa (56 psi) and the feed leaving the membranes was at a pressure of 13 KPa (2 psi). During the run a portion of the feed was circulated through the heat exchanger to ensure that the feed entering the membranes was below 32°C (90°F). The inlet and outlet pressures, temperature, permeate flowrate and volume of feed in the feed tank were monitored every half hour. The conductivity of the UF "feed" (consisting of original feed and recirculated concentrate) and UF permeate were taken once during every run. After each run the concentrate remaining in the membranes was drained back into the feed tank and the membranes flushed with reverse osmosis permeate, contained in the wash tank. The membranes were flushed for about 15 minutes.

The RO unit used in this trial was a smaller RO system than the mobile system used in the initial work at the petroleum spill site. Figure 4 is a schematic of the RO unit used in the demonstration. The system contained one 4 x 40 Toray membrane. The operating pressure used was approximately 5480 KPa (800 psi) and the permeate to concentrate ratio was approximately 8 to 1. The permeate produced was discharged or collected and stored in the wash tank of the UF system to be used for flushing the membrane after each UF run. The concentrate from the RO unit was sent to a single carbon adsorption column.

The carbon column used for this test was 22 cm in diameter and was filled to a depth of 84 cm with 13 kg of Calgon Filtrasorb 400 granular activated carbon. The hydraulic loading to the column was maintained at approximately 0.16 m/h and an EBCT of 31 minutes.

System Performance

Figure 5 shows the UF permeate flowrate for the trial period. The permeate rate dropped very rapidly over the first hours from 7.5L/min to approximately 3.5L/min. This initial drop in rate is a predictable phenomenon resulting from the compaction of the membrane material. Throughout the remainder of the trial the permeate rate remained at 3.5L/min which is a membrane flux rate of $2.7m^3/m^2$/day (68GFD). This flux rate was better than the expected flux of $2.0m^3/m^2$/day and might be expected to decline somewhat upon extended use. The intended purpose of the UF pretreatment unit was for the removal of suspended solids and oil and grease from the RO feed. Tables 1 and 2 show the UF feed before concentration, the UF concentrate after 10:1 concentration , the UF permeate (RO feed) and the percent removal of contaminant in the UF unit (percent of concentration in UF feed - concentration in UF permeate/concentration in UF feed) for total suspended solids (TSS) and for oil and grease. As shown in Table 2 the UF unit removed an average of 63% of the suspended solids and concentrated them to approximately 6 times the feed concentration. After the initial acclimization period the UF unit reduced the TSS to levels of less than 0.2 mg/L. During the acclimization period suspended solids appeared to permeate the UF membrane. The UF permeate from the final batch processed (July 8) also had a high TSS concentration relative to the previous days. Furthermore, in the first and last batches the concentrate TSS concentration was less than two times the feed concentration. This indicated that TSS was not being concentrated effectively during these batches.

As shown in Table 3 an average of 57% of the oil and grease was removed in the UF process and concentrated to 5 times the feed concentration in the final concentrate. The effectiveness of oil and grease removal improved over the initial acclimization period.

To meet the mass balance in a membrane system the concentration in the concentrate should be equal to the concentration in the feed minus the concentration in the permeate times the concentration factor if there is no deposit of contaminants or change in the parameter in the process. For TSS and oil and grease the mass balance for the trial average is within analytical error. However, the mass balance for the individual batches were poor. This is likely due to the wide fluctuations in the quality of the feed. These fluctuations and the fact that TSS and oil and grease are not homogeneously distributed resulted in some batches where the analysis indicated higher oil and grease or suspended solids concentrations in the permeate than in the feed.

Table 3 shows the average concentrations of total organic carbon (TOC) and specific volatile organics for the UF pretreatment trial. The average removal of TOC through the UF unit was 14%. The TOC removed is most likely suspended organic material such as suspended oil or organics adsorbed on suspended material such as clays.

Rejection across the UF membrane was observed for all specific organics observed. The average rejection for benzene was 78%, for toluene was 38%, for xylenes was 66%, and for ethylbenzene was 58%. UF membranes are not expected to reject dissolved molecules under 20,000 MW. Therefore, the observed rejection of these specific organics are likely the result of rejection of solid particles with the organic materials adsorbed on the surface.

In order to assess the effectiveness of the UF pretreatment on the RO process the RO was operated at a concentration factor of eight to one (twice the concentration factor of any previous work at the site) where the permeate flow was held at 8 L/min and the concentrate at 1 L/min by varying the required pressure. The pressure was monitored to indicate any fouling that may have occurred. As the UF unit used could not supply sufficient UF permeate to feed the RO continuously the RO unit was not operated constantly. However, the RO unit was not flushed or washed during the trial.

The pressure and flowrates for the trial are shown in Figure 6. The figure shows that with UF pretreatment a concentration factor of eight to one could be maintained with an average process pressure of 4520 KPa (660 psi). The pressure was relatively constant, rising slightly over the course of the trial.

The concentrations of TSS in the RO feed, the RO permeate and the RO concentrate (Adsorption feed) are shown in Table 1. As expected the removal of TSS across the RO unit approached 100%. The ratio of TSS concentration in the RO concentrate (Adsorption Feed) with respect to the RO feed was much greater than 8:1 which would be expected if the only suspended solids in the concentrate were originally present in the feed. This indicates that solids were generated in the RO process as a result of concentration of dissolved species past their equilibrium solubility limit. This could cause problems if the solids were to remain in the membrane module, however, in this trial this did not appear to occur to any significant extent, as evidenced by the relatively stable required pressure.

As shown in Table 2, oil and grease were well removed in the RO unit. After the first day the oil and grease in the RO permeate was less than 0.5mg/L. The high level of oil and grease in the permeate on the first day may have been a residual from previous trials involving the test system.

The results in Table 3 show that the TOC was well and consistantly removed. The average removal was 82% over the six days of the trial which compared favourably with the average 76% removal observed in the trial without UF pretreatment.

The average percent removal of benzene was 77%, toluene was 86%, xylenes was 96% and ethylbenzene was 93%. These results are slightly better than the removals achieved with RO alone. Furthermore, the final RO permeate quality is better due to the additional removal in the UF unit.

During this short trial adsorption breakthrough of organic contaminants was not expected in the carbon column effluent. The results in Tables 2 and 3 show that oil and grease and all specific volatile organic contaminants were reduced to levels less than the analytical detection limits throughout the trial. The TOC was well removed except for a low level of non-adsorbable residual (less than 10 mg/L) in the column effluent.

The carbon column was observed to act as a granular filter for suspended solids removal. As shown in Table 1 suspended solids were very low in the column effluent, after the initial sample, but began to break through after the first four days. Granular carbon columns have been used in wastewater processing for removal of suspended solids, however backwashing systems are required to maintain effectiveness.

The UF pretreatment trial showed that UF processing can remove suspended solids and oil and grease from contaminated waters prior to RO processing. The UF process is resistant to fouling and prevents fouling in the RO system. This trial indicates that a better quality final effluent can be achieved with UF pretreatment with considerably less operational difficulties. In order to establish the best conditions for UF operation including the best UF membrane type, flushing and washing protocols, concentrate treatment, etc. more trials are necessary.

Spill Clean-up System Design and Cost

The experience accummulated during the spill cleanup tests at Gloucester and at the petroleum site was used as the basis for the design of a spill cleanup system. The design considerations took into account the problems encountered during these tests and incorporated their solutions. The schematic diagram of the system is shown in Figure 7.

The aqueous spill is pumped from the spill containment area (ditch, tank, well, etc.) by a submersible centrifugal pump to the coalescing filter where the immiscible organic layer is separated from the water, then through a multi- media filter to remove most of the suspended materials. The filter backwash is sent back to the spill containment area or to a temporary storage tank for settling. The system is designed with two filters in parallel, one is in the operating mode and the other is on standby. When the operating filter is plugged the flow is switched to the second filter and the first one is backwashed. The filters are switched such that there is always a clean filter on standby.

The filtrate is then pumped through the UF system. A 5u disposable filter cartridge preceeds the UF to protect the membrane. The UF concentrate is returned to the multi media filter to remove agglomerated suspended matter that may buildup. There is an option to return all or part of the UF concentrate to the spill containment area.

The UF permeate is passed through the RO system. The RO permeate may be discharged to a sewer or surface water depending upon its quality with respect to environmental regulations. The RO concentrate is allowed to pass through the activated carbon system.

The activated carbon system consists of 4 columns in parallel, 2 in the operating mode and 2 on standby. When the operating columns are exhausted the flow is switched over to the second set of columns and the carbon replaced in the first set. Operating in this way there is always a set of columns containing fresh carbon. The effluent of the carbon columns may be discharged to a sewer or surface water body. It is not expected that the carbon columns will require backwash as set up in this total system as all suspended matter will have been removed prior to the carbon treatment.

The specifications of major components are shown in Table 4:

Cost

The costs for the system are shown in Table 5. The costs are within ± 20% based on ZENON selling prices in 1987.

The capital cost includes the items described above including the initial charge of membranes and activated carbon and miscellaneous items such interconnecting plumbing and electricals.

The operation and maintenance (O&M) costs include routine maintenance and replacement of activated carbon (1.0 g/L utilization) and cartridge filters. Membrane replacement has not bee included in the O&M costs as the membrane life will be dependent on the spill characteristics.

The cost of the complete system as described here is \$130,000. The cost of O&M is expected to be \$265 per day or \$7.36/m^3 if operated continuously for 150 days a year. Shorter sporadic operations will increase the cost of O&M.

Conclusions

i) Ultrafiltration was shown to be effective for the pretreatment of highly fouling raw feed prior to RO processing. The UF process is resistent to fouling and prevents fouling in the RO system. Better quality final effluent can be achieved with UF pretreatment with considerably less operational difficulties.

ii) The experience accummulated during the demonstrations at Gloucester and at the petroleum site was used as the basis of a portable environmental clean-up system. The system incorporates reverse osmosis and carbon adsorption with optional ultrafiltration pretreatment. The capital cost of the complete system producing 36,000 L/day of treated effluent would be \$130,000 while the operating and maintenance cost would be \$265/day of operation.

References

H. Donison, H. Whittaker, J. Tremblay and R. Putton, "Development and Demonstration of a Mobile Reverse Osmosis/Adsorption Treatment System for Environmental Clean-ups", In: Proceedings of the Technical Seminar on Chemical Spills, Toronto, Ontario, February 1987.

TABLE 1

Concentration of Total Suspended Solids in UF Pretreatment Trial

Date	UF Batch #	UF Feed (mg/L)	UF Concentrate (mg/L)	RO Feed (mg/L)	RO Permeate (mg/L)	Adsorption Feed (mg/L)	Carbon Effluent (mg/L)	% Removal UF	% Removal RO
3 July	1	NA	110	15	<.2	56	97	NA	100%
4 July	2	26	94	47	0.8	110	6	-	98%
5 July	3	84	480	<.2	<.2	160	7	100%	-
6 July	4	3	320	<.2	<.2	15	14	100%	-
7 July	5	12	410	<.2	16 *	98	48	100%	-
8 July	6	95	140	37	<.2	59	40	61%	100%
AVERAGE		44	259	17	<.2	83	35	63%	100%

NA indicates not available

* suspected sample contamination

TABLE 2

Concentration of Oil and Grease in UF Pretreatment Trial

Date	UF Batch #	UF Feed (mg/L)	UF Concentrate (mg/L)	RO Feed (mg/L)	RO Permeate (mg/L)	Adsorption Feed (mg/L)	Carbon Effluent (mg/L)	% Removal UF	% Removal RO
3 July	1	NA	23	10	8	76	<0.5	NA	20%
4 July	2	3	31	10	<0.5	53	<0.5	-	100%
5 July	3	17	13	<0.5	<0.5	14	<0.5	100%	-
6 July	4	9	99	<0.5	<0.5	19	4	100%	-
7 July	5	2	68	4	<0.5	33	<0.5	-	100%
8 July	6	16	51	2	<0.5	13	<0.5	85%	100%
AVERAGE		9	48	4	1	35	1	57%	67%

NA indicates not available

TABLE 3

AVERAGE CONCENTRATION OF ORGANICS IN UF PRETREATMENT TRIAL

Compound	UF Feed (mg/L)	RO Feed (mg/L)	RO Permeate (mg/L)	Adsorption Feed (mg/L)	Carbon Effluent (mg/L)	% Removal UF	% Removal RO
TOC	37	32	5.9	227	11	14%	82%
Benzene	1.05	0.23	0.05	0.83	ND	78%	77%
Toluene	0.13	0.084	0.012	0.207	ND	38%	86%
Xylenes	3.12	1.06	0.04	1.76	ND	66%	96%
Ethylbenzene	0.17	0.07	0.005	0.138	ND	58%	93%

TABLE 4
SPECIFICATIONS OF MAJOR COMPONENTS

Oil/Water separator:

- coalescing type gravity separator
- 50 L/min capacity

Multimedia filters:

- 24" x 72" FRP pressure vessel
- centrifugal pump; 50 L/min at 205 KPa (30 psi)
- media; sand and anthracite 1 m in depth
- filtration hydraulic loading; 8 m/hr
- backwash centrifugal pump; 100-150 L/min at 30 psi
- backwash hydraulic loading 10-24 m/hr

UF System

- ZENON model UFS 5680
- spiral wound polysulphone membrane with 20,000-30,000 molecular weight cut off
- permeate flow; 40 L/min
- operating pressure; 342 KPa (50 psi)

- included: feed pump, valves and controls, 5 u disposable filters cartridge
- skid mounted complete system
- materials of wetted surfaces: 316 stainless steel and polyethylene.

RO System

- ZENON model MF 3150
- eight Toray PEC 1000 high pressure membranes
- 75% expected recovery (depending upon feed quality and operation)
- permeate flow 30 L/min
- operating pressure: up to 5480 KPa (800 psi)
- included: feed pump, valves and controls
- skid mounted complete system
- materials of wetted surfaces: 316 stainless steel and polyethylene

TABLE 4
SPECIFICATIONS OF MAJOR COMPONENTS
(continued)

Activated Carbon System
- 61 cm x 183 cm (24" x 72") FRP pressure vessels
- expected flowrate: 9 L/min
- column hydraulic loading 0.5 m/h
- column EBCT: 60 min.
- carbon bed depth: 1m
- each column contains 146 kg carbon
- breakthrough between 6 days (2.5 g/L carbon utilization) and 4 weeks (0.5 g/L carbon utilization) continuous operation
- operating mode: downflow

TABLE 5
COST OF THE SPILL CLEANUP SYSTEM

Subcomponent	Capital Cost $	O&M Cost $/day
1) Coalescing filter	13,600	18
2) Multimedia filter	4,400	6
3) UF system	35,000	47
4) RO system	51,000	68
5) AC system	9,510	8
AC replacement in 2 columns (once every 14 days)	-------	117
	$113,510	265
Miscellaneous	17,026	
TOTAL	$130,536	

FIGURE 1

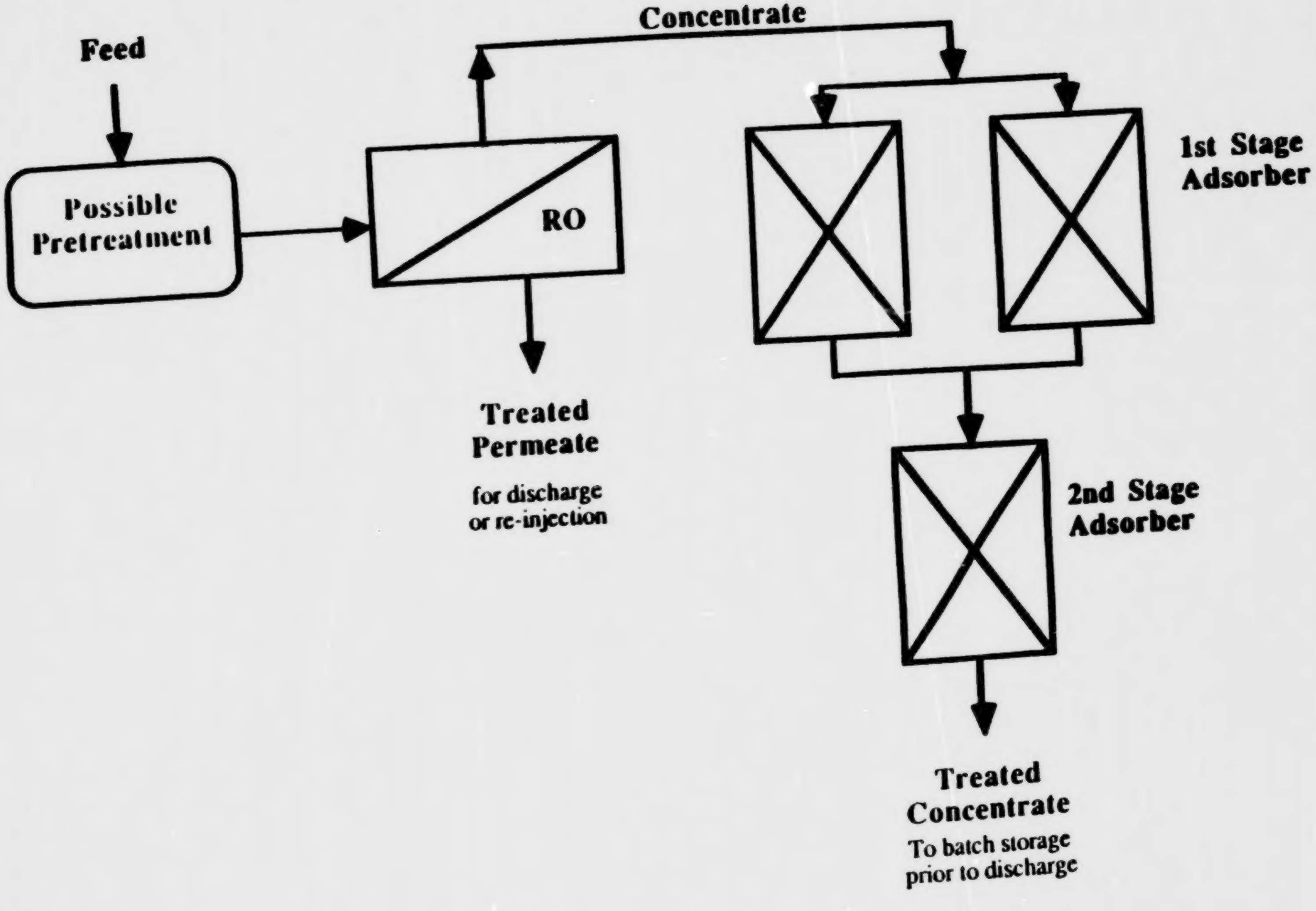

Feed
Possible Pretreatment
RO
Concentrate
1st Stage Adsorber
2nd Stage Adsorber
Treated Permeate
for discharge or re-injection
Treated Concentrate
To batch storage prior to discharge

FIGURE 2

SYSTEM SCHEMATIC OF UF PRETREATMENT FOR RO and ADSORPTION SYSTEM

2 - 9 JULY 1986

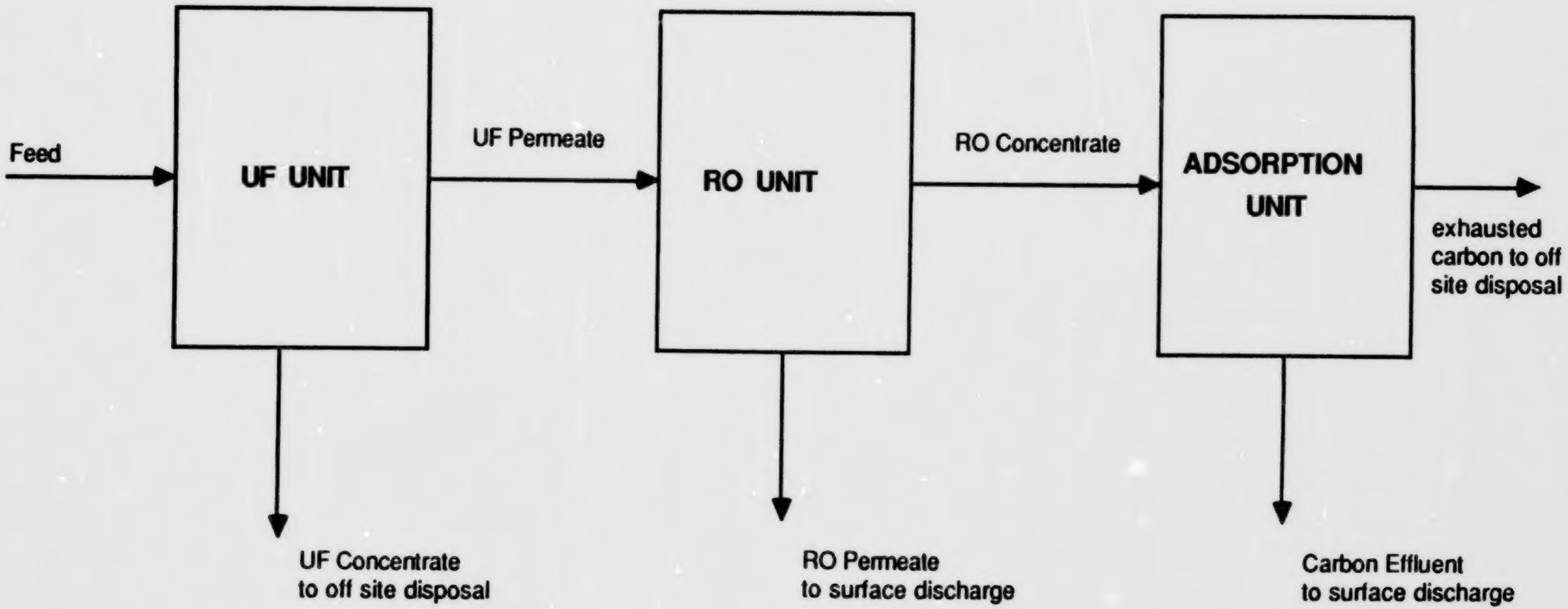
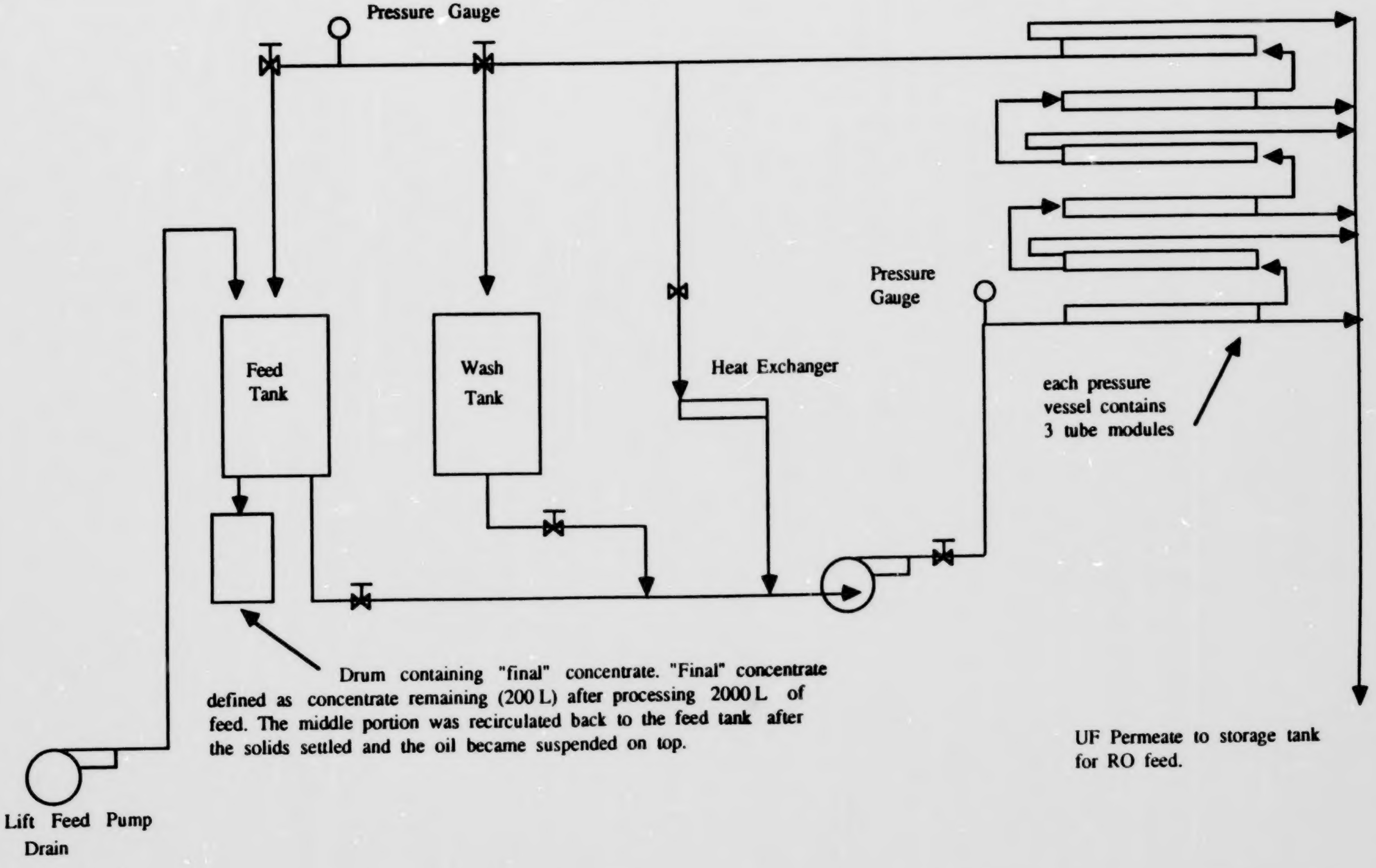

Feed
UF UNIT
UF Permeate
RO UNIT
RO Concentrate
ADSORPTION UNIT
exhausted carbon to off site disposal
UF Concentrate to off site disposal
RO Permeate to surface discharge
Carbon Effluent to surface discharge

FIGURE 3

UF Pretreatment System

2-9 July 1986


Pressure Gauge
Pressure Gauge
Heat Exchanger
Feed Tank
Wash Tank
Lift Feed Pump Drain

each pressure vessel contains 3 tube modules

Drum containing "final" concentrate. "Final" concentrate defined as concentrate remaining (200 L) after processing 2000 L of feed. The middle portion was recirculated back to the feed tank after the solids settled and the oil became suspended on top.

UF Permeate to storage tank for RO feed.

FIGURE 4

RO "LAB" UNIT and ADSORPTION UNIT

2 - 9 JULY 1986

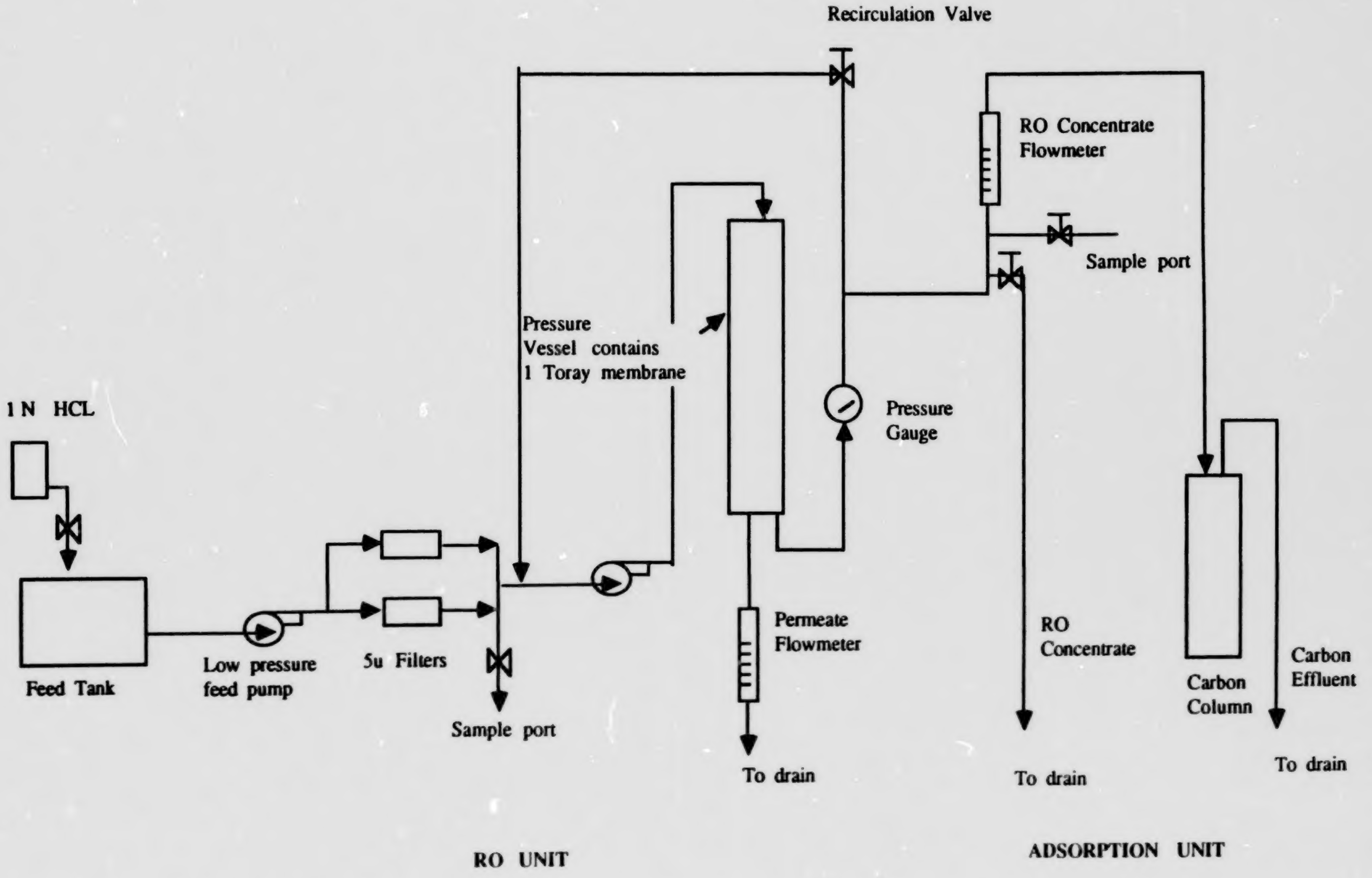
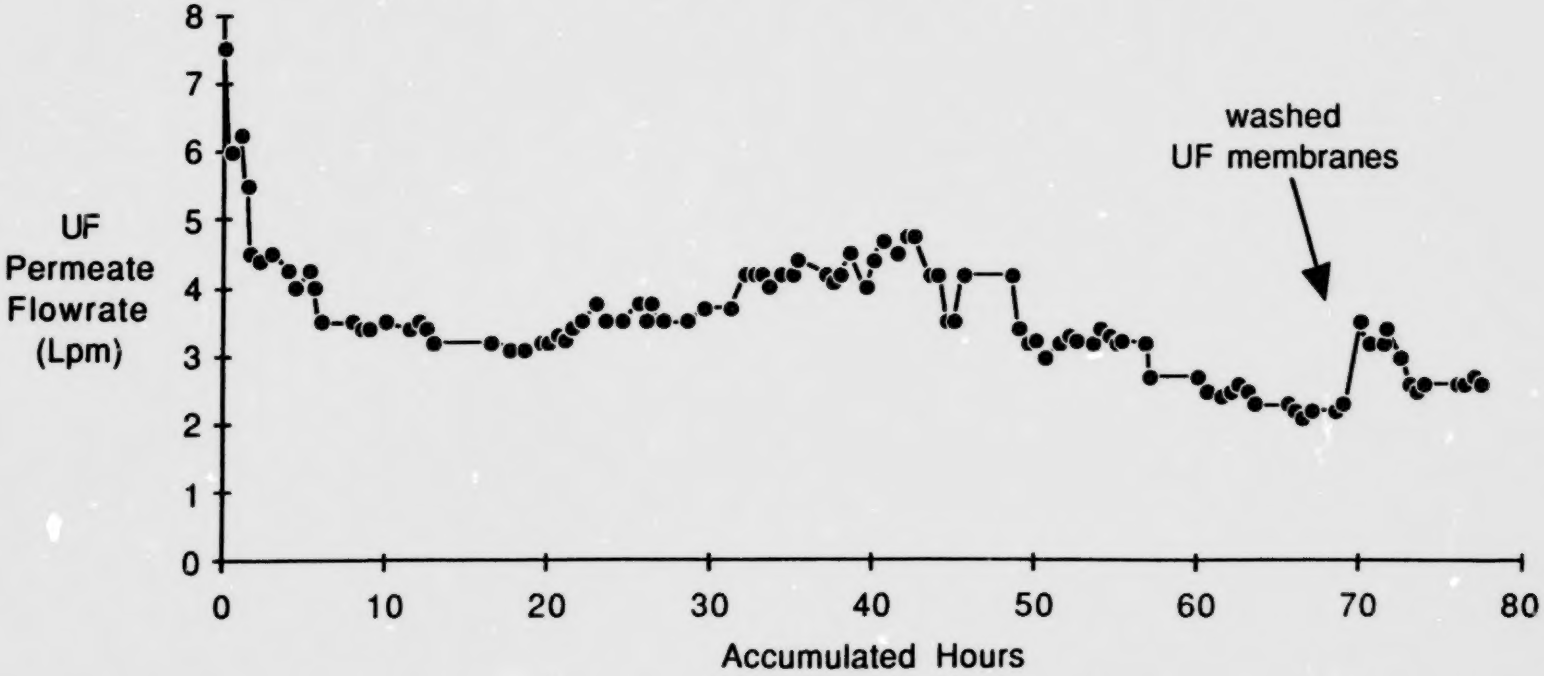

Recirculation Valve
RO Concentrate Flowmeter
Sample port
Pressure Vessel contains 1 Toray membrane
1 N HCL
Pressure Gauge
Feed Tank
Low pressure feed pump
5u Filters
Sample port
Permeate Flowmeter
To drain
RO Concentrate
To drain
Carbon Column
Carbon Effluent
To drain
RO UNIT
ADSORPTION UNIT

FIGURE 5

UF Permeate Flowrate



Note: Dotted line represents the end of batch concentration runs involving processing of 2000 L of petroleum spill drainage water.

FIGURE 6

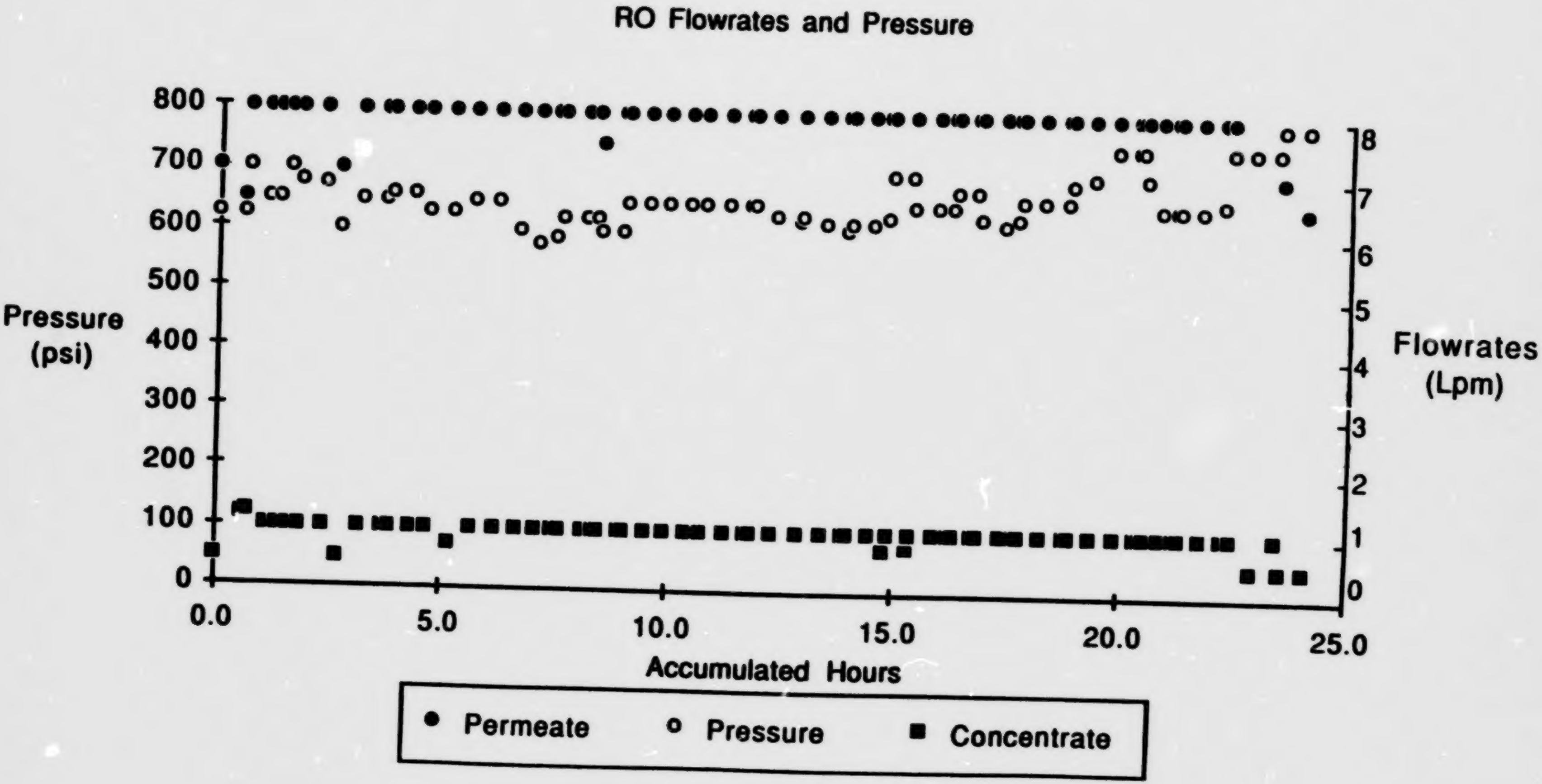
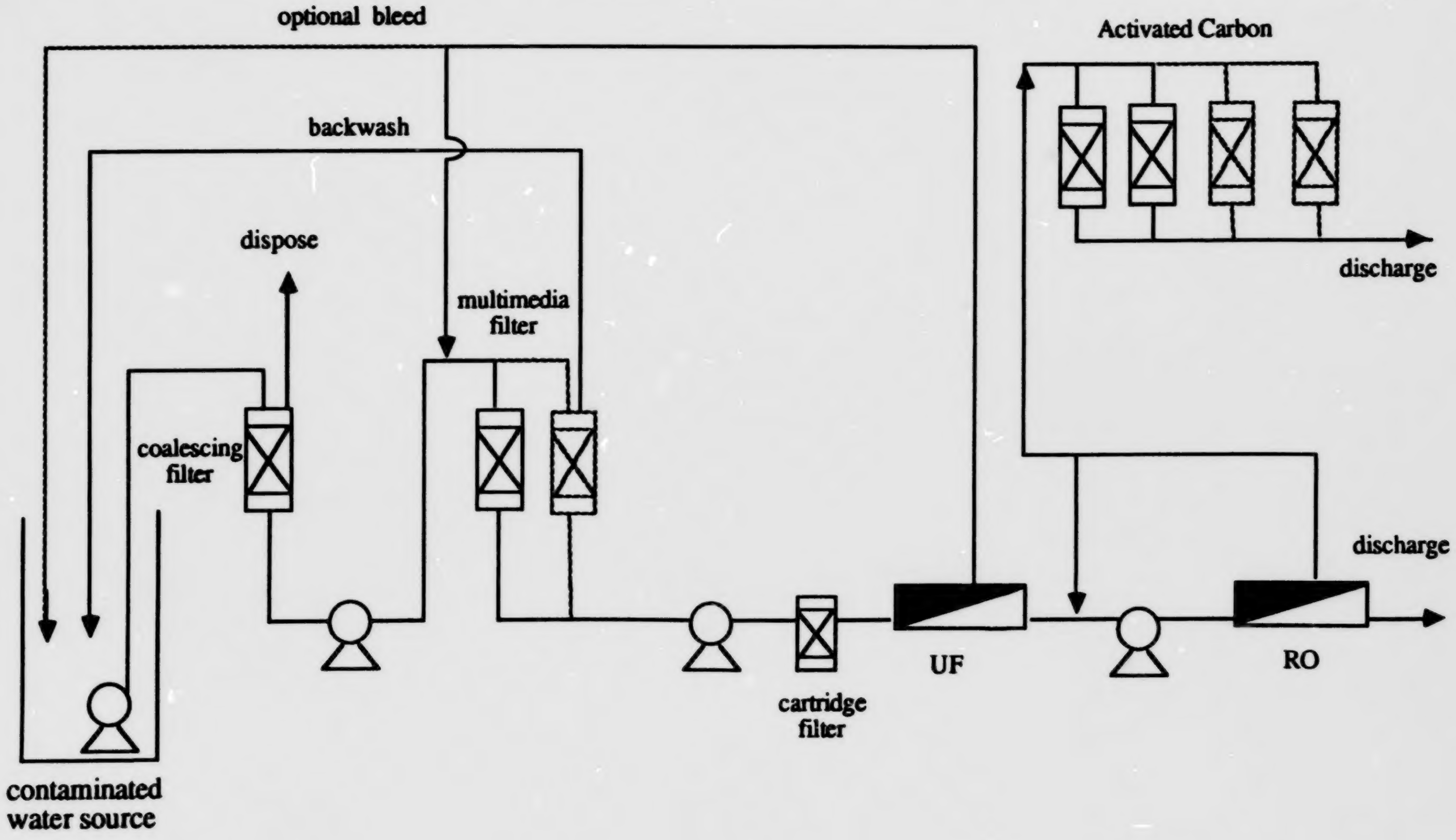

RO Flowrates and Pressure
Pressure (psi)
800
700
600
500
400
300
200
100
0
0.0
5.0
10.0
15.0
20.0
25.0
Accumulated Hours
Flowrates (Lpm)
8
7
6
5
4
3
2
1
0
● Permeate
o Pressure
■ Concentrate

FIGURE 7

Schematic of the Spill Clean up System


optional bleed
backwash
dispose
coalescing filter
multimedia filter
Activated Carbon
discharge
discharge
UF
cartridge filter
RO
contaminated water source

IDENTIFICATION OF POTENTIAL LEAKS BY HAZARD & OPERABILITY STUDIES

R.E. Knowlton
Chemetics International Company

ABSTRACT

Guide Word Hazard & Operability Studies are a powerful tool for identifying hazards caused by deviations within a specific unit. However, they may not identify hazards which are caused by "interactions" between units which are not connected from a process point of view but are in close proximity as built. Hazards caused by interactions between a unit and its environment may also be missed.

This paper describes how, in a real example, a combination of Guide Word & Creative Checklist Hazard & Operabilty Studies was used to identify potential hazards which could be caused by both deviations and interactions. Although the methodology would identify all types of hazards and operational difficulties, the main emphasis was on the identification of potential leaks. The nature of the materials in this example was such that the principal hazards which could arise from leaks were fire and explosion. However, the same methodology can be applied to the detection of leaks which could lead to other types of hazards such as the consequences of the leakage of toxic materials.

INTRODUCTION

In the ideal world, all accidents would be anticipated at the design stage of a chemical plant and all the causes removed. The chemical industry is continually striving to achieve this ideal. However, in the real world accidents still occur. On a few, fortunately rare occasions, accidents occur which have such significant consequences, that the senior management of major companies initiate programs to ensure that the chances of similar accidents occuring within their own organization are significantly reduced.

One such keynote disaster occured at a place called Flixborough in England where the explosion of cyclohexane vapor mixed with air devastated a complete plant and some of the surrounding area. This disaster had the following consequences in the Pharmaceuticals Division of Imperial Chemical Industries in the UK in 1974.

i) Training programs on Hazard & Operability studies were developed for team members, senior management and in particular Hazard & Operability Study Leaders.

ii) A comprehensive program to apply Hazard & Operability Studies on existing facilities was initiated.

iii) A procedure was developed to ensure that plant modifications received a safety check before they were implemented.

iv) The existing Hazard & Operability Studies based on Guide Words, were enhanced to include a methodology which would identify hazardous interactions between units which were separate from a process point of view, but were in close proximity as built. Hazards to or from the environment and a unit would also be identified.

This paper concentrates on the enhancement of Hazard & Operability Studies to include interactions.

The main thrust of the post-Flixborough activities was directed against identification of potential fires and explosions. However, as any external leak of a flammable process material would mix with air and sooner or later contact a source of ignition, the Hazard & Operability Studies were directed towards the identification of leaks.

SUBJECT OF THIS STUDY

This study was concerned with the identification of potential leaks in the supply of fuel to the boiler and gas turbines which provided heat and electrical power to a UK production unit of ICI Pharmaceuticals Division.

The site contained units for bulk drug production, various formulation units, packaging, warehousing and various laboratory and service facilities.

The fuels concerned were natural gas and fuel oil, each of which could supply both the boilers and the gas turbines. For simplicity, only the details relevant to this study will be described and illustrated.

Natural gas from a utility (British Gas) was reduced in pressure from the main supply pressure of about 350 psig to 95 psig in a let-down station located close to an underground main supply line. This was in a field about 1/4 mile from the plant site. The let down system was built above ground and surrounded by a nine feet high metal fence with a locked entrance gate. The gate could only be opened by British Gas personnel.

The gas line then passed South, buried to a depth of several feet under a field until after it entered the plant site. There was an above ground section of line mounted on concrete posts which were set in the banks of a canal for a distance of 200 yards. The pipeline then turned west, passed under a road and continued underground for a further distance of about 200 yards. The pipeline turned North, was taken above ground to a second let down station mounted on the surface adjacent to two liquid nitrogen storage tanks. This let down station which contained the first ICI isolation valve, reduced the pressure from 95 to 80 psig. The final run of pipe was over a dyked area containing the fuel oil storage tanks and into a building containing the boilers and gas turbines.

The oil storage consisted of seven vertical cylindrical storage tanks mounted about five feet below grade level in a dyked area next to the boiler house. The storage tanks were connected to the boiler house by pumps and lines.

There was an incinerator across a road from the liquid nitrogen storage tanks and wooden cooling towers next to the incinerator.

The layout is shown in Figure 1.

DEFINITION FOR THE HAZARD & OPERABILITY STUDY

The Battery Limits

The battery limits for the first phase of the study and which is covered by this paper were as follows:

The natural gas line was to be studied from the point where it left the first let down station to the point where it entered the boiler house.

The fuel oil tanks were to be studied from the inlet hose to the tanks to the point where the fuel oil entered the boiler house.

The fuel oil tankers were to be studied from the point where the loaded tankers entered the local roadway until they left the local roadway empty.

The Scope of the Study

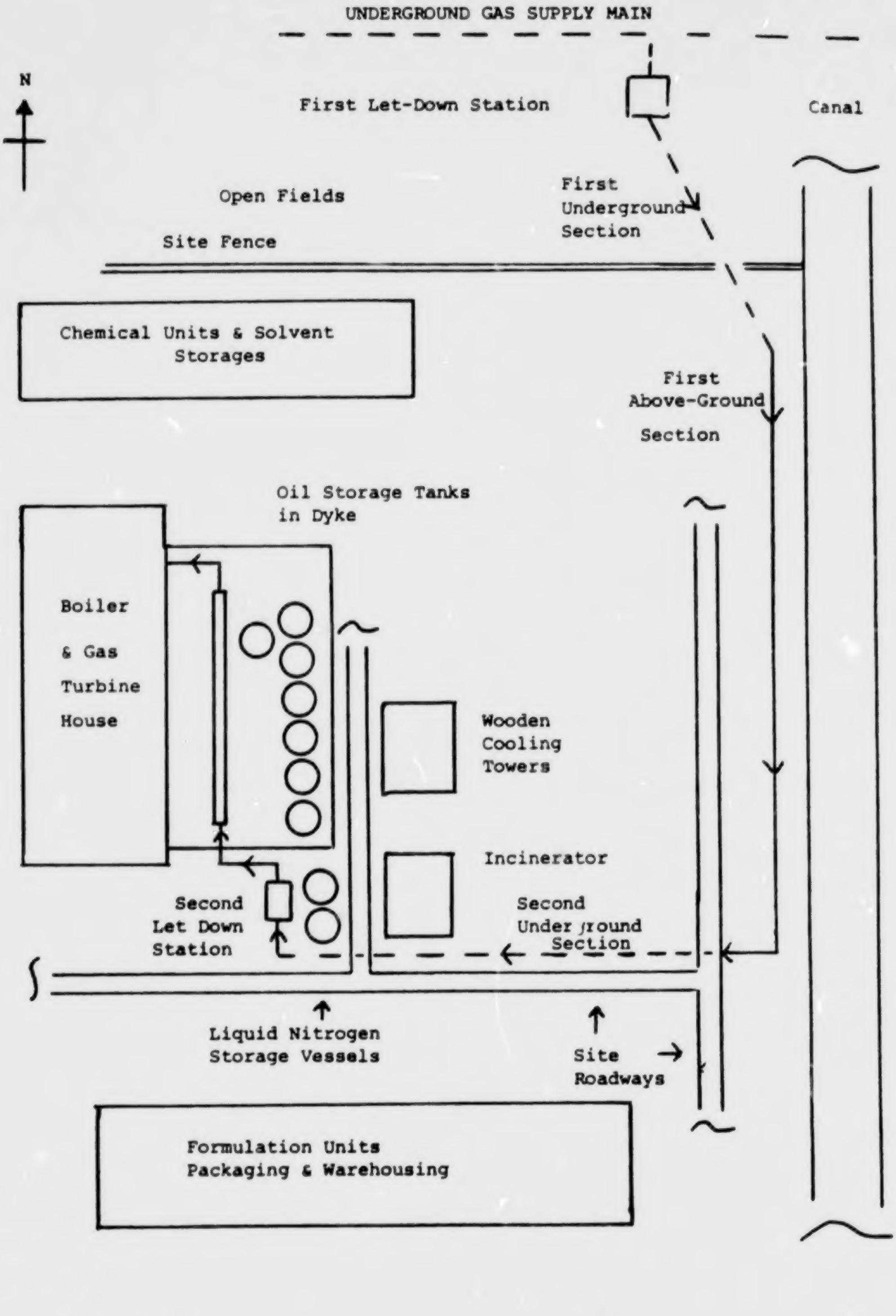
The study had to consider not only the hazards caused by maloperation and malfunction of the individual systems but also any interactions between the gas line, oil tanks and anything in the vicinity which could give rise to hazards - particularly fire and explosion.

There was potential for interactions between the following:

- Off road traffic
- Road traffic
- Canal traffic
- Air traffic

FIGURE 1 GAS SUPPLY & OIL STORAGE

NOT TO SCALE


UNDERGROUND GAS SUPPLY MAIN
N
First Let-Down Station
Canal
Open Fields
First Underground Section
Site Fence
Chemical Units & Solvent Storages
First Above-Ground Section
Oil Storage Tanks in Dyke
Boiler & Gas Turbine House
Wooden Cooling Towers
Incinerator
Second Let Down Station
Second Underground Section
Liquid Nitrogen Storage Vessels
Site Roadways
Formulation Units Packaging & Warehousing

- Ground condition
- Natural occurences e.g. lightning, meteorites
- Gas line
- Oil tanks and lines
- Liquid nitrogen storage
- Boiler house
- Incinerator
- Wooden cooling towers

The Team

The team consisted of the following:

- Five engineers of various disciplines
- A safety advisor
- A study secretary
- A Hazop study leader

METHODOLOGY

It was realized from the definition, that a Guide Word Hazard & Operability Study, although necessary, would not be sufficient to ensure comprehensive coverage. The following procedure was developed and adopted.

Decide Top Event

With the background disaster of Flixborough in mind, it was clear that attention should be drawn in particular to fire and explosion. However, it was decided to investigate the precursors to these hazards, which lead rapidly to the conclusion that the "top event" to be identified was a significant leak of hydrocarbon. Any leaks would mix with air and sooner or later would contact a source of ignition.

Create a Checklist

Having decided the top event, a checklist was prepared of external and interactive events which could lead to this top event. The type of checklist used is given in Figure 2.

FIGURE 2 - CHECKLIST FOR INTERACTIONS

Off road traffic
Road traffic
Canal traffic
Air traffic
Vessel Failures
Building Failures
Burst Service Mains
Canal bank failure
Subsidence
Civil work
Corrosion
Over pressure

Explosions
Fires
Ice
Low temperature
Static
Lightning
Meteorite
Tipping & storage
Maloperation
Valdalism
Terrorism

Execute Guide Word Hazard & Operability Studies

The Guide Word Studies were carried out next for the following reasons:

The Guide Word methodology would ensure that all the members of the team would have a clear idea of the function of every part of the units.

The Guide Word Studies would reveal not only direct hazards & operability problems but also deviations which, in isolation might appear harmless but which in specific locations, could lead to significant hazards by interactions.

Further details on Guide Word Hazard & Operability Studies are given in References 1 & 2.

Creative Checklist Study

Armed with both the checklist derived earlier and the data from the Guide Word studies, the team would carry out an on site inspection of each part of the facility, looking for interactions. A description of Creative Checklist Hazard & Operability Studies is given in Reference 2.

Follow Up on the Identified Hazards

This would be carried out as usual once all the hazards had been identified.

RESULTS

Summary of Results & Time Taken

In aggregate, the team identified a total of 273 hazards during ten, half day Hazop examination sessions. A summary of the hazards detected for the major plant items, the type of examination which detected them and the time taken are below.

Plant Items	Number of Hazards Detected by		Time in Team Days For	
	Guide Word	Checklist	Guide Word	Check List
Gas Pipeline	115	71	2½	½
Oil Storage	39	36	1½	½
Oil Tankers	-	12	-	
Totals	154	119	4	1

From the above, 56% of the hazards were detected by Guide Words and 44% by the checklist. The Guide Word studies detected hazards at the typical rate of 20 per half day.

The Checklist studies detected hazards at the very high average rate of about 60 per half day. This high rate was due in part to the in-depth appreciation of the function of every piece of equipment and its possible deviations, which had already been achieved by the preceding Guide Word studies.

Sometimes the understanding of a potential hazard was only fully understood by the combination of both types of examinations.

Details of Selected Specific Hazards

Here are some specific details:

i) Absence of Rapid & Effective Means of Isolation for the Gas Pipeline. One of the oil storage tanks was fitted with an inlet dip-leg which reached almost to the bottom of the tank to avoid splash-fill. There was no syphon breaker. The inlet valve and the coupling to fit the tanker hose were mounted on the dyke wall and could discharge oil outside the dyke. The Guide Word study identified this possibility of reverse flow.

On site inspection carried out during the Checklist study showed that oil spillage could flow down a road and be ignited by the incinerator. The side of the incinerator building which faced the liquid nitrogen storage vessels had large open doors and plastic windows. Any fire in the incinerator building would radiate heat to the liquid nitrogen storage vessels area. Any liquid nitrogen spillage could flow down to the natural gas main and cause it to split by brittle fracture.

The only isolation valve accessible to ICI personnel was a diaphragm valve downstream of this possible leakage point. If the natural gas line had a leakage upstream of the isolation, the only remedy was to telephone the gas utility. It typically took half an hour to make the connection. The gas utility would then dispatch an operator in a truck who would drive to the site, unlock the let-down station and manually isolate the gas supply. This response would take another half hour. Although this particular scenario was not very likely, it did indicate that the emergency shut off procedure was deficient. Other scenarios were identified which gave similar results.

ii) Lack of Control of Dumping of Corrosives. The underground sections of pipe were wrapped and cathodically protected against corrosion. Inspection of the first underground section, coupled with the checklist item "corrosion" revealed that waste corrosive materials were being dumped on the surface of the ground, above the run of the pipe. There was no "dumping of corrosives" control procedure.

iii) Danger from Road Traffic. The pipeline was taken underground for the second underground section at a point within a few inches of the roadway. This was identified as a potential hazard by the checklist item "road traffic". However, events accelerated the followup in this instance. Close to the roadway was a small concrete pillar which contained the terminals which enabled the cathodic protection to be checked. During the Hazop examination, a truck reversed into this pillar and smashed it. The truck could just as easily have reversed into the gas pipeline and caused a leak upstream of the accessible isolation valve. Although it is normal practice to complete the hazard identification prior to taking action, on this occasion the problem was too urgent. The following three-stage followup actions were taken:

a) Immediately, staging was erected around the pipeline to afford some protection from traffic.
b) A "freeway" type barrier was obtained and installed within two weeks.
c) As part of the final followup, the entire in-plant pipeline was re-routed away from the road and with a remote controlled, slam-shut valve installed at the point where the pipe emerged from the first underground section.

iv) Locked pressure explosion of the pipeline in the oil storage area. The section of pipe which ran through the dyked oil tank area had a greatly increased cross sectional area. This feature was designed to give increased capacity to assist a control system. The enlarged section of pipe had slam shut valves at each end. These valves would trap a significant quantity of gas locked in under pressure in the event of an emergency shut down. A fire in the dyked area could overheat the gas causing the pipeline to burst. A block and bleed valve avoided this possibility.

v) Hazards from Oil Tanker Movements. It was found that loaded tankers were pulling off the road and adjacent to the dyke wall. The roadway was about five feet higher than the dyked area. The dyke wall had not been designed to withstand the tanker weight and it was thought possible for a tanker to fall into the dyked area. Subsequent calculations carried out by the civil engineers showed that the dyke wall had adequate strength. The tankers on entering and leaving the loading area tended to cut the corner where the liquid nitrogen tanks were located. This could lead to damage to a liquid nitrogen line with results which have already been discussed. A freeway type barrier was erected.

FOLLOW-UP TO THIS PHASE

Further Hazard & Operability Studies were carried out on the incinerator, nitrogen system etc. One subsequent Hazard & Operability Study which required yet more technique development was the application of Hazard & Operability Studies to the entire plant road traffic system. A description of this study will be included in a planned advanced book on Hazard & Operability Studies.

CONCLUSIONS

1. An intense examination of relatively simple pieces of plant, in this case a piece of pipe and some small oil storage tanks, can identify a large number of hazards.
2. The Guide Word examination although necessary, is not sufficient to identify all hazards when these are caused by "interaction" between separate units or between a unit and its environment.
3. The combination of Guide Word and Checklist Hazard & Operability Studies appears to provide a comprehensive, cost-effective method of Hazard Identification. The Checklist Study only added 20% to the total team time devoted to Hazard Identification.
4. When dealing with an existing unit, a Guide Word examination followed by a Checklist examination is an effective sequence of examination.

ACKNOWLEDGEMENTS

The data generated by a Hazard & Operability Study are normally regarded as "privileged". Hazards, once identified, may appear to be so obvious that the ability of the design team may be suspect. No such conclusions should be drawn. The permission of the client, ICI Pharmaceuticals Division to publish this paper is gratefully acknowledged.

The enthusiastic participation of the team members for this study was greatly appreciated.

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NEW JERSEY'S ACCIDENTAL RELEASE PREVENTION PROGRAM

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INTRODUCTION

No one will dispute the need for comprehensive accidental release prevention programs in the chemical process industry. The long history of major accidents in the chemical and allied products industry points out the need for aggressive action in the field of release prevention. That history includes the now famous incidents which have occurred in Flixborough, United Kingdom; Seveso, Italy; Bhopal, India; and Institute, West Virginia, U.S.A.

This paper will describe a release prevention program sponsored by a New Jersey legislator, endorsed by the New Jersey Chemical Industry Council, signed by New Jersey Governor Thomas H. Kean and now being implemented by the New Jersey Department of Environmental Protection.

BACKGROUND

With a land area of 7500 square miles and a population of 7.5 million, New Jersey is one of the most densely populated and highly industrialized states in the U.S.A., employing more people in the chemical manufacturing industry than any other state in the nation. New Jersey is also the second largest producer of chemicals in the country, with 75% of its residents living near chemical manufacturing industries. Several other factors contributed to the sense of urgency with which we adopted a release prevention program.

Since the industrial revolution, our state has been a leader in attracting new chemical and manufacturing industries. Following World War II, an unprecedented industrial growth occurred in New Jersey, with residential areas developing immediately adjacent to neighborhood chemical plants. Although the close proximity of residence and workplace was attractive to workers, this very common arrangement denied the community the simple advantage of a buffer zone. Today, many of our state's major chemical and petrochemical facilities are surrounded by highly populated areas. Add to this the fact that many of our facilities are old, approaching the 35 year mark, and while age itself should not be the basis of acceptability, it is certainly true that older facilities, without proper maintenance, present far greater risks than the newer or well-cared-for processes.

Second, imported chemicals have placed considerable pressure on the marketplace in this country. In response, chemical facilities in our state have responded with increased productivity, improved efficiency, and, unfortunately, deferred capital improvement programs. Also, facilities in our state have switched from the production of feedstock chemicals, which are now being produced more cheaply in other plants, to specialty chemicals. Adaptation of existing process equipment from original design purpose to some altered configuration is rather common. This, of course, changes margins of safety incorporated in the original designs and correspondingly increases the chance of an accidental release.

Third, we recognize that many of our manufacturing and storage facilities which handle extraordinarily hazardous chemicals are not the large, multi-national corporations. In fact, the greatest inventory of many of these hazardous chemicals is handled by small, privately-owned firms with typically fewer than twenty employees. While it is true that the large facilities have some form of risk management program, it is also true that many of the small facilities lack even the rudiments of an industrial safety effort. Of further concern, many of the small facilities, operating without benefit of a risk management program, are located immediately within residential communities, a disastrous potential.

The chemical industry argues that their safety record is exemplary, in fact, the best of all manufacturing industries. We must be careful to understand how the safety statistics are determined. They are based on worker health and safety, missed workdays, loss prevention and other equivalent measures. No place in this scorecard are the acute effects on a community of the releases from rupture disks or pressure relief systems. In fact, engineers traditionally approached safety design features with workers in mind. Today, in every chemical facility in the world, this fact is clearly evident in the thousands of pressure relief systems that discharge directly to the atmosphere. This is very protective of the workers, but not so for the surrounding community.

Statistics also point to the need for more improved release prevention programs. Across the U.S.A., almost 24,000 notifications of sudden accidental releases were made to the United States Environmental Protection Agency's National Response Center during the 27 month time period between January 1983 and March 1985. That amounts to almost 900 notifications per month or almost 30 per day. The most frequently reported hazardous materials reported during that time period include chlorine, anhydrous ammonia, hydrochloric acid and sulfuric acid.

In New Jersey alone, we received notification of over 6,000 releases during the period from 1981-1985. A marked increase in the incidents of these accidental releases occurred between October 1984 and January 1985, with nineteen separate releases occurring. These releases caused hundreds of citizen complaints, and resulted in well over one hundred individuals requesting treatment at area hospitals.

These incidents occurred during the same time period as the Bhopal tragedy, heightening the concerns of both the citizens and the legislature in New Jersey. Immediately, members of the legislature began to work with the Department of Environmental Protection, with valuable input from the New Jersey Chemical Industry Council, on a regulatory program designed to prevent accidental chemical releases. All parties were convinced that a regulatory program was necessary if we were to protect our residents and restore public confidence in government regulators and industry. On January 8, 1986, the Toxic Catastrophe Prevention Act was signed into law.

NEW JERSEY'S RELEASE PREVENTION PROGRAM

The byword of the Toxic Catastrophe Prevention Act (TCPA) is prevention. It requires that a facility owner establish a program to review the current state of operations at facilities handling extraordinarily hazardous substances (EHS), identify those circumstances that could potentially lead to an accidental chemical release, and take the necessary preemptive actions. The Act gives the Department of Environmental Protection the authority to implement a regulatory program and establishes the basic program elements. The basic elements of the program are registration, a risk management program, accident risk assessment, EHS list expansion and a fee schedule.

EXTRAORDINARILY HAZARDOUS SUBSTANCES (EHS)

The Act regulates those facilities which handle, store or manufacture materials defined as extraordinarily hazardous substances (EHS). An EHS is defined as follows:

> "any substance or chemical compound used, manufactured, stored, or capable of being produced from onsite components in this State in sufficient quantities at a single site such that its release into the environment would produce a significant likelihood that persons exposed will suffer acute health effects resulting in death or permanent disability."

Table 1 lists eleven substances identified on the initial EHS list, with the minimum reportable quantity.

TABLE 1. INITIAL EHS LIST

NAME	FORMULA	MINIMUM REPORTABLE QUANTITY, LBS
hydrogen chloride	HCl	2,000
allyl chloride	CH_2CHCH_2Cl	2,000
hydrogen cyanide	HCN	500
hydrogen fluoride	HF	500
chlorine	Cl_2	500
phosphorous trichloride	PCl_3	500
hydrogen sulfide	H_2S	500
phosgene	$COCl_2$	100
bromine	Br_2	100
methyl isocyanate	MIC	100
toluene-2,4-diisocyanate	TDI	100

Any facility in New Jersey that uses, handles, stores or is capable of producing one of these EHS's in quantities equal to or greater than the reportable quantity is subject to the provisions of TCPA. The only exemption allowed in the Act is for research and development laboratories.

REGISTRATION

During the winter of 1986, the Department developed and issued registration forms to facilities throughout the state who were potentially affected by the program. The registration form includes information such as facility identification, EHS inventory, process description and listing of principal equipment, a profile of the surrounding area and the names of all insurance carriers underwriting the facility's environmental liability and workers' compensation insurance policies.

In total, 1,865 registration forms were returned to the Department from which the universe of affected sites was defined. Industrial facilities, potable water treatment facilities, and wastewater treatment facilities were the major categories that registered with us. The facilities which returned the registration forms are divided between EHS and non-EHS facilities. An "EHS facility" was defined as one which reported having the reportable quantity of an EHS as specified by the Act. A "Non-EHS facility" was defined as one which either reported that the EHS was present in quantities less than the reportable quantity or that no EHS was handled at the facility. A total of 804 facilities have registered and are subject to the TCPA program requirements. These statistics are summarized in Figure 1.

Registrants were also requested to indicate if a risk management program is in place. As shown in Figure 2, 86% of the industrial facilities indicated that they currently have risk management programs, while only 59% of the potable and wastewater treatment facilities indicated the existence of a risk management program. The quality of the risk management programs is undetermined since the regulations requesting their submission and review have not yet been finalized.

RISK MANAGEMENT PROGRAM (RMP)

The approach inherent in the TCPA program is to allow facilities with established RMP's to use those plans to comply with the law. TCPA defines an RMP as an eight-point program consisting of requirements for: safety reviews of new and existing equipment, standard operating procedures, preventive maintenance programs, operator training, accident investigations, risk assessment of specific pieces of equipment, emergency response planning, and audits.

1. Safety Review

The requirement for safety reviews for new, existing and modified equipment is a key component of an RMP. It is based on the premise that basic designs of chemical processing equipment are presented in established codes or based on established practice and that these codes and practices must be followed. Many codes and standards have been developed by engineers and manufacturers from experience with hazardous chemicals. The Department developed the term "criteria for design and operation" to refer to this body of knowledge. The term, means any code, consensus or governmentally mandated standard applicable to the particular EHS facility's design and operation. It also includes documented guidelines, practices or procedures adopted by a facility when codes and standards are nonexistent or need supplementation. These guidelines, practices or procedures must be based on sound engineering practices supported by documentation demonstrating their successful application to the particular EHS process in question. Additionally, the most current technology that will result in significant reduction of risk, or state of the art, should be considered for design.

It is important to note that safety reviews are required for all modifications. We recognize that modifications can be a major cause of accidents because in many cases they may be improperly engineered or unauthorized. For example, a temporary pipe installed at the Nypro Factory in Flixborough, United Kingdom, in 1974, failed two months later and caused the release of over 50 tons of cyclohexane, which exploded and killed 28 people. The modification was poorly engineered and was in violation of two British design standards.

We require safety reviews to be conducted annually, during which the actual conditions will be compared to the approved process and istrument drawings and operating conditions. The actual equipment will be inspected and facility personnel interviewed to determine that actual conditions do not deviate from the approved design drawings and/or approved operating conditions. The inspection will also verify that all safety relief devices and emergency systems such as deluges, interlocks, back-up systems and alarms are functioning or capable of functioning as designed. Any deficiencies must be corrected immediately. The annual safety review is a form of audit to insure that the risk management program is being fully implemented at the day to day operational level of the facility.

2. Standard Operating Procedures

The development of, and adherence to standard operating procedures is a fundamental of safe facility operation. To be effective, procedures must address material safety, process hazards, and critical safety steps and should be readily available to all personnel.

The Department has required that standard operating procedures include a definition of operational practices regarding process materials and conditions; normal, abnormal and emergency conditions, pre-startup, startup, shutdown, safety devices, sampling, safety, maintenance, recordkeeping and staffing. The documentation of standard operating procedures is expected to be a compilation or set of manuals.

The Department, as part of its review of the facility's risk management program, will verify that the operating procedures actually in use by the chemical operator, conform to the standards set by the Department and the facility's risk management program. The Department has already had experience where the actual SOP in use did not begin to meet the standards set by the facility's corporate level managers. Through inspections, the

Department will ensure that the actual SOP's are complete and the operators using them are intimately familiar with their contents.

3. Preventive Maintenance Program

The policies and practices for maintenance varies considerably among industrial facilities. Policy may range from "breakdown" maintenance only, to extensive preventive maintenance and predictive maintenance. The purpose of the preventive maintenance requirements is to reduce EHS accidents resulting from improperly maintained, tested, or inspected equipment.

An approvable RMP will require that the preventive maintenance program insure that only modifications that have been approved and authorized by a responsible manager are made and that communications are maintained between the maintenance, production, safety and engineering departments.

Inspection, testing and repair of EHS equipment will prevent failures and thus, prevent accidental releases. The preventive maintenance program will include requirements for internal or external inspections, testing and checks of equipment, pressure safety devices and safety instrumentation and a schedule for checking each piece of EHS equipment. Equipment inspection schedules will be based on equipment histories, suppliers' recommendations, standards of the industry, or corrosion rates. Inspecting or testing of pressure safety devices will be based on the facility's criteria for design and operation unless it does not exist, in which case inspecting or testing will be performed annually. The frequency of testing or inspection of pressure relief devices will be at intervals adequate to insure the reliable operation of these devices and should be set forth in the criteria for design and operation. Testing and inspection frequency of safety instrumentation such as interlocks, alarms and shutdown devices will depend on the EHS being handled and the hazard that would result in the event of instrument failure. Some safety devices are so critical that testing weekly or before each batch will be required.

The RMP requirements for a preventive maintenance program must also include an information management and retrieval system for the preventive maintenance program. Specifically, documentation of all inspection reports, testing and training information will be required. In addition, a system must be established for maintaining accurate records of all inspections, breakdowns, repairs and replacements of EHS equipment with the means for data retrieval and analysis necessary to perform equipment reliability studies. The reliability studies will be used to formulate estimates of repair and replacement frequencies for particular equipment.

These studies will then be used to determine if the preventative maintenance program is truly achieving its goals and will highlight what areas need adjustments to be made in the actual maintenance schedules. The generation of actual on-site facility specific data will greatly enhance the facility's ability to forecast and control maintenance operations.

The data generated in the reliability studies will also provide a base to be used when the facility conducts a probabilistic risk assessment to determine the frequency with which a release may occur as the result of an equipment failure.

4. Operating Training

Current practices in operator training range from working with an experienced operator for a period of time to structured and rigorous training. Many studies, including reports of incidents which have occurred in New Jersey, confirm that industrial accidents are frequently caused by acts of individuals involved in the accident, either directly or indirectly. Thus, initial training and maintenance of a level of knowledge and skill are essential to safe operation and the prevention of accidents. The purpose of the operator training program is to make the operators aware of the hazards under which they operate, as well as to teach them how to perform their jobs.

The Department's requirements for the operator training program state that the program must be written and include job descriptions, types and lengths of training, performance evaluation and recordkeeping. The Department specifically requires that three types of training programs be implemented. These are: 1) a general orientation program that is generic to site and is used to provide the employee with general safety information regarding the site. 2) Training on specific EHS activities that will permit the employee to carry out his work assignment and perform it in a safe manner. This program may be a combination of classroom training and on the job "hands on" experience. It may include equipment familiarization, operating data collection and entry, start-up and shut down procedures, control and adjustment of operating conditions, and the application of standard operating procedures to actual conditions. 3) The third category of training required is that of annual refresher training to provide an overview and updated information on all aspects of the employees job functions. In addition, the operator training program will provide a mechanism for testing the trainee. The evaluation can be based on oral and written tests and a demonstration of ability to perform the job. The purpose of the evaluation is to insure that the trainee is qualified to assume the responsibility for operation of the EHS facility.

5. Accident Investigation Procedures

Thorough accident reporting and investigation at chemical plants are usually conducted for those accidents in which people are injured or property is damaged. The TCPA program defines an EHS accident as "an unplanned, unforeseen or unintended incident, situation, condition or set of circumstances which results in a direct or indirect EHS release." The purpose of accident investigation procedures are to determine the many factors contributing to the accident, the corrective actions necessary to prevent a recurrence and to have all personnel learn from the information compiled.

The Department will require that procedures for investigating accidents must be written and include: identification of those persons investigating and reporting accidents, a schedule for initiating EHS accident investigations, requirements for reporting and recordkeeping, and methods for implementing recommendations. The reports shall be reviewed with site personnel.

The RMP accident investigation procedures will also require a system for recordkeeping of unanticipated and unusual events. Recordkeeping includes accident reports, monthly status reports of all recommendations for corrective action, a list of personnel involved in EHS accidents and an annual summary report. The report will be used to discover patterns or trends, if any, of actual releases, near misses, human errors and equipment failures. These requirements emphasize that one purpose of investigations is to make certain that all personnel learn from the results of the investigation. The results of the accident reports are required to be made a part of the facilities training program so that all employees may learn from the experiences of others.

6. Risk Assessment Program

TCPA recognizes the fact that modern technology, operating systems and safeguards can fail to protect the public against an accidental chemical release. The element of the TCPA risk management program designed to identify potential accidents is "risk assessment of specific pieces of equipment and operating alternatives." The purpose of this element of the RMP is to provide a systematic examination of an actual or proposed facility in order to identify, evaluate and mitigate potential accidents. This portion of an RMP is divided into two parts: a hazard analysis and a risk assessment. This division is in accord with the work of CONCAWE (the oil companies study group for conservation of Clean Air and Water, Europe) and the Center for Chemical Process Safety of the American Institute for Chemical Engineers. The basis of hazard analysis and risk assessment is to obtain answers to the questions:

a. What can go wrong (accident scenario)?

b. How can it go wrong (accident paths)?

c. How likely is it (the probability of the accident scenarios)?

d. What is the potential damage (the consequence of the accident)?

e. What can be done to reduce the likelihood or consequence of the accident scenario (risk reduction efforts or mitigating measures)?

A hazard analysis is a qualitative identification of conditions that may result in an accident. Risk assessment is a powerful tool which quantifies the probability of a hazard and the consequences for the purpose of risk reduction.

The Department's regulations will require that a hazard analysis be conducted on all new facilities, new operating alternatives and modifications. A hazard analysis is defined as "a systematic identification of the potential conditions that may result in an EHS accident using singly or in combination a Hazard and Operability Study (HAZOP), Failure Mode and

Effect Analysis (FMEA), qualitative Fault Tree Analysis (FTA), or What If/Check List." These techniques have been established as the standard, accepted methods in the work of the Center for Process Safety, CONCAWE, and the World Bank. Other common terms synonymous with hazard analysis include hazard survey and hazard identification. The complexity of a process or lack of information on the design of new equipment or operating procedures frequently results in the creation of hazards. Similarly, hazards are created by modifications to process conditions, operating procedures and equipment. A hazard analysis may also be necessary when a process is sufficiently unique or new and little or no experience, standards, or guidelines exist to identify and control the hazard. The different hazard analysis techniques identified above are used to predict the effects on the process and equipment from variations in conditions such as temperature, pressure, and composition, in addition to hazards such as toxicity, corrosivity, and explosivity. The proposed procedures will require that the criticality of the potential release be ranked and actions for mitigating the consequences of the hazards be taken. The hazard analysis techniques permit identification of hazards before the EHS is handled at the facility. The results can then be incorporated into the design and operation of the facility.

The RMP requires that the hazard analysis be conducted every three years on existing EHS facilities. The hazard analysis must be conducted by a qualified team comprised of the registrant's staff, an outside qualified consultant chosen by the facility or by a combination thereof. The team must have sufficient knowledge, experience and authority to make meaningful contributions to the hazard analysis.

In those cases where the hazard analysis shows that there is a potential for a release in the amount of five times the reportable quantity for that EHS, a formal risk assessment will be required. A release potential of five times the reportable quantity is considered significantly more serious and warrants the application of a more rigorous process of risk assessment.

The formal risk assessment will include 1) an estimate of the release quantity, 2) a dispersion analysis, 3) a consequence analysis, 4) an estimate of the probability of the release, 5) an evaluation of the state of the art, and 6) the preparation of a risk reduction plan.

7. Emergency Response Planning

The Department recognizes that a strengthened capacity to minimize and abate releases once they occur and efficient plans to evacuate people in the surrounding community if those releases cannot be contained are vital components of a comprehensive community safety program and mandates that emergency response be an element of an effective risk management program. It is impossible to eliminate all chances of an accidental release; emergency response procedures are needed at EHS facilities in order to reduce or mitigate the effects of a release on the surrounding community. These requirements emphasize that emergency response planning involves both the EHS site and the surrounding community. EHS facility owners have the responsibility to disseminate information to the community regarding the

EHS, the potential risks to the public, the preventive measures in place and their emergency response capabilities.

The emergency response plan must include a description and location of EHSs at the site, a list of the emergency response equipment and supplies, and the name and title of the site emergency coordinator and alternates, and requirements for the emergency notification system in the event of an accident. In addition, the requirements include procedures, phone numbers, and information required to report an emergency to the Department, a detailed plan of evacuation for onsite personnel, and a plan for re-entry of the facility and site recovery. Re-entry and site recovery requirements include procedures and equipment for the safe cleanup, decontamination, and removal of hazardous materials.

8. Audit Requirements

Most chemical facilities are familiar with procedures for conducting safety and environmental audits. An audit is a mechanism for self-enforcement at the facility. The purpose is to insure that all elements of the program are being planned, scheduled, updated and executed in compliance with the RMP.

This element of the RMP requires that the facility establish requirements for auditing which shall include 1) the audit scope and procedures and 2) minimum qualifications for audit team personnel. An audit team consists of those persons who perform the audits and shall be employees of the registrant or an independent consultant. Only a minority of the members of the audit team may be involved in the day to day operation or management of the specific EHS facility being audited to insure an objective and unbiased audit.

The Department also requires as a part of the faciiities annual report that an audit checklist be completed by the facility. This checklist, prepared by the Department, essentially requires the facility to report the status of compliance of its risk management program with each of the requirements that the Department has established for its program. This audit checklist is required to be certified by both the highest ranking official on site and by a principal executive officer of the corporation. This procedure ensures that the issue of risk management is brought to the attention of the corporate level management.

ACCIDENT RISK ASSESSMENT

The TCPA program has a different regulatory strategy for those facilities that do not have existing programs for managing their EHS operations. Facilities that do not have established risk management programs are essentially considered to pose an unknown risk, and are therefore required to undergo a detailed accident risk assessment conducted by an independent third party.

The blueprint for the accident risk assessment is a workplan which is developed by the Department. The workplan will serve as the basis for the accident risk assessment and will include:

- verification of the EHS inventory
- safety review and engineering assessment of all EHS equipment
- review of the preventive maintenance program
- evaluation of any existing secondary containment device
- hazard analysis
- a review of alternate processes or procedures that would reduce risk
- review of operator training programs
- an evaluation of the emergency response capabilities

The Department has by regulation established the minimum requirements for a generic workplan for EHS facilities. The actual workplan for each facility will be a modification of the generic plan adopted to the specific needs of the facility to be evaluated. These modifications will be made by the department in co-operation with the affected facility.

The actual risk assessment must be conducted by the Department or an independent consultant selected by the Department.

Implementation of the workplan will result in the development of an EHS accident risk assessment report. The report will identify any deficiencies found and identify recommendations for corrective actions. The Department will review the accident risk assessment report and develop a risk reduction plan. The plan will identify all required remedial actions and a timetable for implementation. Completion of the risk reduction plan will result in the development of a risk management program.

Clearly the fact that the accident risk assessment must be conducted by an independent consultant serves as an incentive for facilities to develop their own risk management programs. In either case, however, the outcome is the development and implementation of a facility specific risk management program.

The RMP, once approved by the Department, is considered to be a viable document and will serve as the facility's bible in managing the day-to-day risks inherent in handling an EHS. In order to ensure that the RMP remains current and continues to be implemented by the facility, the Department has set requirements for annual reporting. Among other items, the annual report will include the results of the facility's audit of its RMP and the detailed program checklist.

INSPECTIONS

The Department, as part of the implementation of the TCPA, will be conducting inspections of the affected facilities. As part of the initial review of the facilities RMP, the Department will conduct an on-site inspection to determine that the actual implementation of the risk management program conforms to that which was submitted to the Department. This inspection may include enforcement inspections, review of maintenance and training records, and interviews with facility employees to determine the training and operating procedures are actually being practiced as written. Once a facilities RMP has been approved, the Department will make routine inspections to verify that remedial actions are occurring as required and that the RMP continues to be an on-going program.

The Department will also conduct investigations as the result of accidental releases. These investigations will be used to determine the cause of the incident and to determine what steps can be taken to prevent similar incidents from occurring in the future. The program is a prevention program and thus the inspections must be used to acquire its knowledge necessary to prevent future incidents.

EHS LIST EXPANSION

The Department is required by law to expand the initial EHS list and add any additional materials which meet the definition of extraordinarily hazardous substances. The enabling legislation required that this effort be completed within eighteen months. In developing the first phase of the list expansion the Department focused on two main criteria: volatility and toxicity. The ratio of these two criterion were used to develop a Substance Hazard Index (SHI). Substance Hazard Index values were calculated for all chemicals reviewed, compared to the lowest SHI from the original list of 11 EHS's (excluding toluene-2,4-diisocyanate) and used to develop the first phase of the list expansion.

1. Substance Hazard Index

For each chemical with available data on toxicity and vapor pressure, a Substance Hazard Index (SHI) was calculated. Properties of toxicity and volatility may be combined using a modification of the Vapor Hazard Ratio as given in Fundamentals of Industrial Hygiene (Second Edition), edited by Julian B. Olishifski, published by the National Safety Council, Copyright 1979 (pg. 144). The proposed SHI is defined as follows:

$$\text{SHI} = \frac{\text{Equilibrium Vapor Concentration at } 20^\circ\text{C (ppm)}}{\text{Acute Toxicity Concentration (ppm)}} \qquad (1)$$

Equilibrium vapor concentration, EVC, at 20°C (ppm) may be calculated by the following:

$$\text{EVC} = \frac{\text{Vapor Pressure of Substance at } 20^\circ\text{C} \times 10^6}{\text{Total Atmospheric Pressure}}$$

For gases and liquids with vapor pressures greater than 760 millimeters of mercury at 20° Celsius, the EVC reduced to 1,000,000 parts per million.

SHI resolves problems inherent in setting limits for toxicity and vapor pressure separately and then deciding the relative weight of each factor. The lowest SHI on the proposed expansion of the EHS List is 1388, which corresponds to the SHI for 36 percent hydrochloric acid, derived from the initial list. This is the highest concentration commercially available and is widely recognized as extremely hazardous. An SHI of 1388 is also the lowest on the initial EHS List, with the exception of toluene-2,4-diisocyanate.

2. EHS List and Data

Using the SHI concept the Department reviewed approximately 3,000 chemicals contained on lists prepared by U.S. Department of Transportation, Seveso Directive, National Fire Protection Association and others. As a result of these reviews, the Department is proposing to add an additional 94 chemicals to the list of extraordinarily hazardous substances.

OTHER REQUIREMENTS

In order for any program of this magnitude to be properly administered by a regulatory agency, it must be provided with adequate funding. The law allowed the Department to develop a fee schedule and collect fees from all affected facilities. All fees collected must be used by the Department directly for program implementation. The intent of the legislation was to allow the Department to implement the program on a self-supporting basis without taking funds from the general revenue.

As the TCPA program develops, the Department also plans on establishing risk determination criteria. This criteria or quantitative standard, will then serve as a benchmark for risk acceptability. The criteria will reflect the size of the potentially exposed population and the gravity of consequence.

CONCLUSION

Accidents undoubtedly will happen, but regulators can assist in minimizing the probability and consequences of those accidents. Regulations can require that practices and procedures based on the experience of the world community be adhered to by all. In addition, regulations will encourage facility owners to make the necessary safety related expenditures. In doing so, the odds of the accident occurring will be reduced.

The goal of this program is to prevent a catastrophe and minimize the effects should one occur. To achieve this goal, the Department is committed to review and evaluation of all risk management programs. The Department is committed to enforcing the standards and principles of this goal through inspections and reporting requirements. The regulator's perspective on accidental release prevention is to embody the principles of community safety in enforceable standards of achievement.

Figure 1. NUMBER OF REGISTERED AND EHS SITES

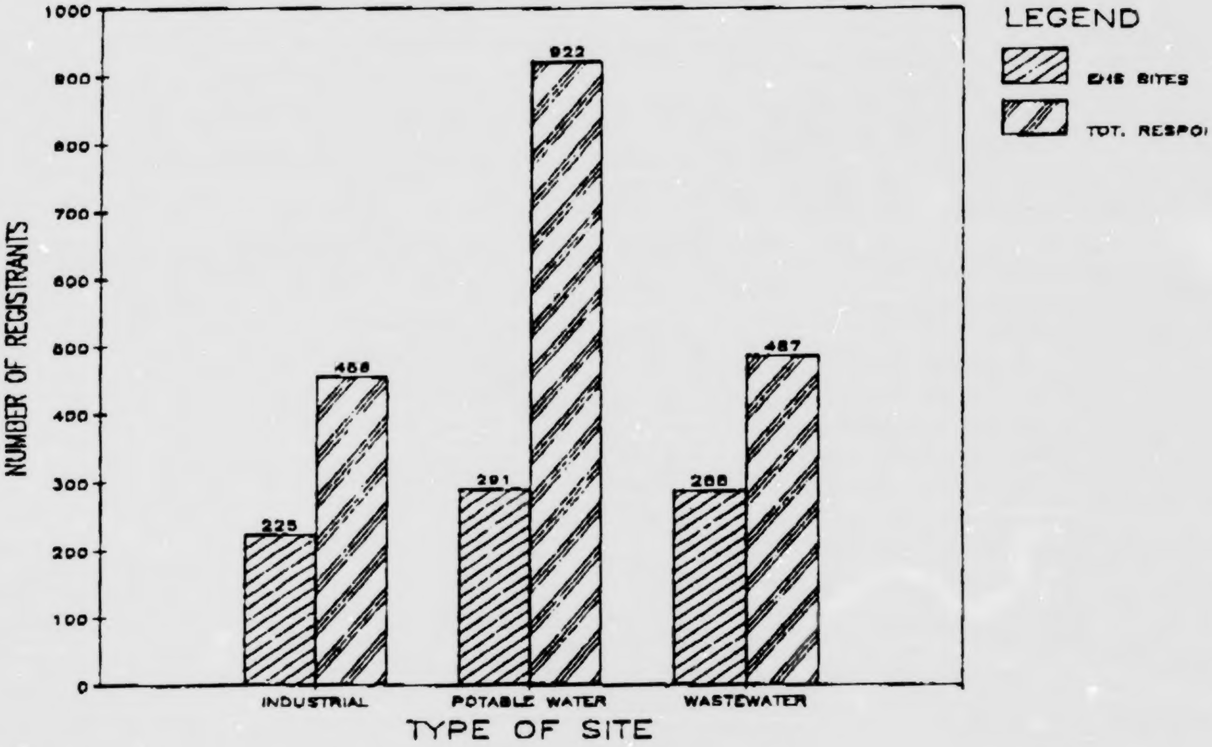
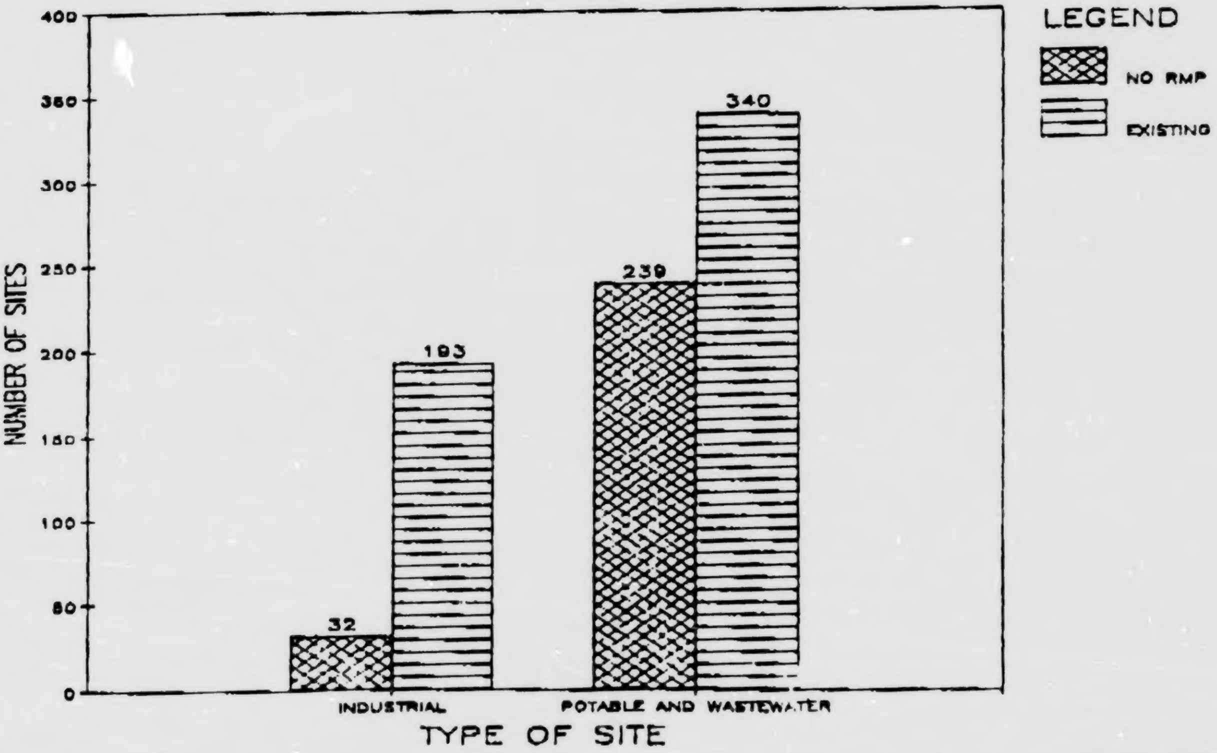


Figure 2. REGISTRANTS REPORTING EXISTENCE OF AN RMP



CAER PROGRAM IMPLEMENTATION

J.A. MYERS
DU PONT CANADA INC.

I AM THE CAER COORDINATOR AT DU PONT CANADA'S MAITLAND SITE. THE SITE IS LOCATED ON THE ST. LAWRENCE RIVER AND SEAWAY BORDERING N.Y. STATE NEAR BROCKVILLE, ONTARIO, 130 MILES WEST OF MONTREAL. OUR PROPERTY RUNS NORTH FROM THE RIVER TO HIGHWAY 401. THE MAIN LINE OF THE CNR BETWEEN MONTREAL AND TORONTO RUNS THROUGH OUR PROPERTY.

WE ARE IN AUGUSTA TOWNSHIP WHICH IS ONE OF THE TWENTY-TWO TOWNSHIPS MAKING UP THE ONTARIO COUNTIES OF LEEDS AND GRENVILLE.

THE SITE EMPLOYS ABOUT 600 PEOPLE IN THE MANUFACTURE OF NYLON INTERMEDIATES, FREON®, SPANDEX FIBRES, ENGINEERING RESINS AND HYDROGEN PEROXIDE. MANY VERY HAZARDOUS CHEMICALS ARE HANDLED AND USED ON OUR SITE. ALSO A FERTILIZER PLANT PRODUCING AND HANDLING LARGE AMOUNTS OF AMMONIA IS LOCATED JUST TO THE WEST.

BECAUSE OF THE NATURE OF OUR RAW MATERIALS AND PRODUCTS WE HAVE HAD TRANSPORTATION EMERGENCY PLANS IN PLACE FOR MANY YEARS. WE ARE THE EASTERN ONTARIO REGIONAL RESPONSE CENTRE FOR THE CCPA TEAP. WE ALSO HAVE A FULLY EQUIPPED AND WELL TRAINED CERT TO MEET OUR TEAP RESPONSIBILITIES AND TO HANDLE CHEMICAL EMERGENCIES FOR ALL OF DU PONT PRODUCTS MADE IN OR IMPORTED INTO CANADA. OUR FOCUS WAS, HOWEVER, TO CONTAIN RISKS WITHIN OUR OWN PROPERTY AND TO ASSUME THAT BECAUSE WE WERE GOOD PEOPLE AND GOOD FOR THE COMMUNITY THAT THE PUBLIC PERCEPTION OF US AND THE CHEMICAL INDUSTRY WOULD BE IN GENERAL, FAVOURABLE.

WE ARE VERY PROUD OF OUR OVERALL SAFETY PERFORMANCE AND OUR ABILITY TO CONTAIN RISKS. THIS DOESN'T MATTER BECAUSE WHAT THE PUBLIC PERCEIVES OF US IS OF OVERRIDING SIGNIFICANCE. THE PUBLIC'S PERCEPTION IS INFLUENCED NOT ONLY BY WHAT HAPPENS IN CANADA BUT AROUND THE WORLD. AS PRACTITIONERS OF SCIENCE AND TECHNOLOGY WE MUST RETAIN CREDIBILITY IF WE ARE TO CONTRIBUTE TO OUR FULLEST POTENTIAL - CREDIBILITY IS THE HEART AND SOUL OF HARD NOSED REALITY!

ALL OF THESE INCIDENTS HAVE CAUSED THE CHEMICAL INDUSTRY TO LOOK AGAIN INWARDLY AT FURTHER RISK REDUCTION AND MORE IMPORTANTLY TO LOOK OUTWARDLY AND WORK HARDER TO EARN THE TRUST OF THE PUBLIC AND TO INDICATE AND DEMONSTRATE THAT WE ARE IN CONTROL.

MY SITE HAS BEEN INVOLVED WITH THE CAER PROGRAM FOR OVER TWO YEARS NOW AND WE THINK THAT IT IS ONE OF THE MOST IMPORTANT PROGRAMS EVER UNDERTAKEN. CAER - COMMUNITY AWARENESS AND EMERGENCY RESPONSE. THE NATURAL AND EASIEST PLACE TO START IS WITH EMERGENCY RESPONSE.

HOWEVER, AS YOU PROCEED IN YOUR PLANNING YOU ARE DRAWN TO RECOGNIZE THE GREAT NEEDS AROUND COMMUNITY AWARENESS AND TO REACH OUT AND TAKE THE MULTITUDE OF OPPORTUNITIES THAT ARE PRESENTED OR GENERATED TO COMMUNICATE TO THE PUBLIC. THE CAER PROGRAM PRESENTS A REAL OPPORTUNITY TO GET INVOLVED IN A MASSIVE COMMUNICATIONS PROCESS.

LET'S GO BACK TO THE BEGINNING.

WE FIRST HEARD ABOUT CAER IN 1985 THROUGH CORPORATE SUPPORT FOR THE U.S. CMA INITIATED PROGRAM. MY BOSS ATTENDED A CAER SEMINAR IN CHICAGO IN 1985-JUNE AND I WAS ASKED TO TAKE ON THE COORDINATION EFFORT AT OUR SITE. WE WERE RECEPTIVE AS WE HAD BEEN SENSITIZED BY BHOPHAL AND BY THE CCPA PUBLIC SURVEY WHICH REFLECTED POORLY ON THE CHEMICAL INDUSTRY. WE HAD ALSO FOUND THROUGH WORKING WITH SOME LOCAL ENVIRONMENTAL GROUPS THAT THERE WAS A SIGNIFICANT NEED TO COMMUNICATE AND PROMOTE UNDERSTANDING BEYOND THE PLANT FENCE. CAER WAS RIGHT FOR US!

WE NEEDED TO CONVINCE THE COMMUNITY THAT CAER WAS RIGHT FOR THEM!

TO START THE PROCESS WE INVITED ALL OF THE ELECTED OFFICIALS AND THE POLICE AND FIRE CHIEFS FROM THE ADJACENT MUNICIPALITIES AND TOWNSHIPS TO A WORKSHOP AT OUR PLANT. THIS WAS HELD IN 1986-JANUARY WITH OVER FORTY IN ATTENDANCE. THE CMA FILM "HAZARDOUS MATERIAL EMERGENCIES" WAS SHOWN FOLLOWED BY A WORKSHOP IN WHICH THE FOLLOWING QUESTIONS WERE PRESENTED:

1. WHAT IS THE CURRENT STATE OF YOUR EMERGENCY RESPONSE CAPABILITY?
2. WHAT WOULD BE THE IDEAL STATE OF EMERGENCY RESPONSE?
3. WHAT WOULD PREVENT US MOVING FORWARD TO THE IDEAL STATE? (I.E., WHAT ARE THE BARRIERS?
4. WHAT IS THE BENEFIT OF MOVING FORWARD? - AND THERE ARE REAL BENEFITS!

THE REPORTOUTS FROM THE WORKSHOP WERE PRESENTED FOLLOWING A RECEPTION AND DINNER AT THE COUNTRY CLUB. THE RESULT OF THE WORKSHOP WAS THE AGREEMENT THAT A NEED DID EXIST FOR A COORDINATED EMERGENCY RESPONSE CAPABILITY IN THE AREA.

THE WORKSHOP WAS A SUCCESS BUT THERE WERE SURPRISES:

- LOCAL POLITICAL RIVALRIES
- FIRE CHIEFS WERE CRYING OUT FOR THIS SUPPORT
- EXISTING EMERGENCY PLANS HAD NEVER BEEN TESTED
- ALL PARTIES SUPPORTIVE
- LEADERSHIP WAS LACKING
- LOCAL EMERGENCY SERVICES UNABLE TO COMMUNICATE TO EACH OTHER
- MUTUAL AID GROUPS ON BOARD IMMEDIATELY
- LACK OF RECOGNITION OF TRANSPORTATION CORRIDORS
- SUPRISED AT STATE OF PREPAREDNESS OF OUR SITE AND OUR CAPABILITY TO RESPOND - VERY RELIEVED

AS A RESULT OF THIS MEETING THE LEEDS AND GRENVILLE EMERGENCY PREPAREDNESS COORDINATING COMMITTEE WAS FORMED. IT'S TASK WAS TO SET UP AND COORDINATE AN EMERGENCY PLAN FOR THE AREA, ORGANIZE DISASTER TESTS AND TO INCREASE COMMUNITY AWARENESS OF POTENTIAL EMERGENCIES.

THE COMMITTEE MET EIGHT TIMES IN 1986 LEADING TO A TEST ON NOVEMBER-20.

INITIALLY A LOT OF TIME WAS SPENT GETTING TO KNOW EACH OTHER AND UNDERSTANDING EACH OTHER'S ROLES AND CAPABILITIES - A VERY GOOD LEARNING PERIOD - FOR EXAMPLE WE FOUND THAT THE COAST GUARD HAD DEPARTMENT OF DEFENSE TRAINED DIVERS AVAILABLE FOR OPP USE, HOW TO CALL OUT THE ARMY, WHO OPERATE THE EMO SIRENS, WHERE AMBULANCES ARE, ETC. ETC.

THE CCPA CAER BOOK WAS A VERY PRACTICAL AND USEFUL GUIDE. THE PERSONS WHO WROTE THIS KNEW WHAT WAS NEEDED.

OF KEY SIGNIFICANCE WAS THE SLOW RECOGNITION BY EVERYONE THAT I WAS ACTING AS A CATALYST - IT WAS THEIR SHOW. AGAIN THIS IS IMPORTANT AS THERE ARE A LOT OF SENSITIVE PEOPLE AROUND WITH TURF TO PROTECT. THERE ARE RIVALRIES BETWEEN POLICE AND FIRE DEPARTMENTS AND BETWEEN LARGE AND SMALL COMMUNITIES. IT TAKES TIME FOR THEM TO DEVELOP CONFIDENCE IN YOUR ROLE. IT IS IMPORTANT TO PERSEVERE AS THERE IS A NEED FOR CAER PROGRAMS IN EVERY COMMUNITY ACROSS THE LAND.

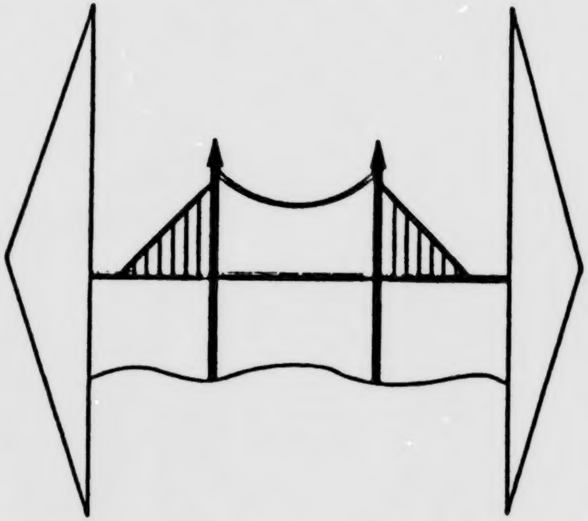
THE RESPONSIBILITY BRIDGE SHOWN IN FIGURE 1 OUTLINES THE ROLES OF ALL THE PARTICIPANTS. WE TRIED TO INVOLVE AS MANY AGENCIES AND JURISDICTIONS AS POSSIBLE WITH MANY GROUPS COMING FORWARD AND ASKING TO BE INVOLVED. THE WARDEN OF THE UNITED COUNTIES WAS APPOINTED AS THE HONORARY CHAIRMAN AND FIGURE 2 'THE ELEMENTS OF INTEREST AROUND AN INCIDENT' SHOWS HOW BROAD THE INVOLVEMENT CAN BECOME.

FIGURE I
RESPONSIBILITY BRIDGE

INDUSTRY RESPONSIBILITIES

1. Assure safe work practices.
2. Assure employees personal safety and the safety of visitors.
3. Establish safety programs.
4. Protect lives and property onsite.
5. Coordinate all plant personnel during an emergency.
6. Develop plans and procedures to respond to emergencies.
7. Provide security, safety equipment, general training, and information on chemical hazards.

COORDINATING GROUP BRIDGING ACTIONS



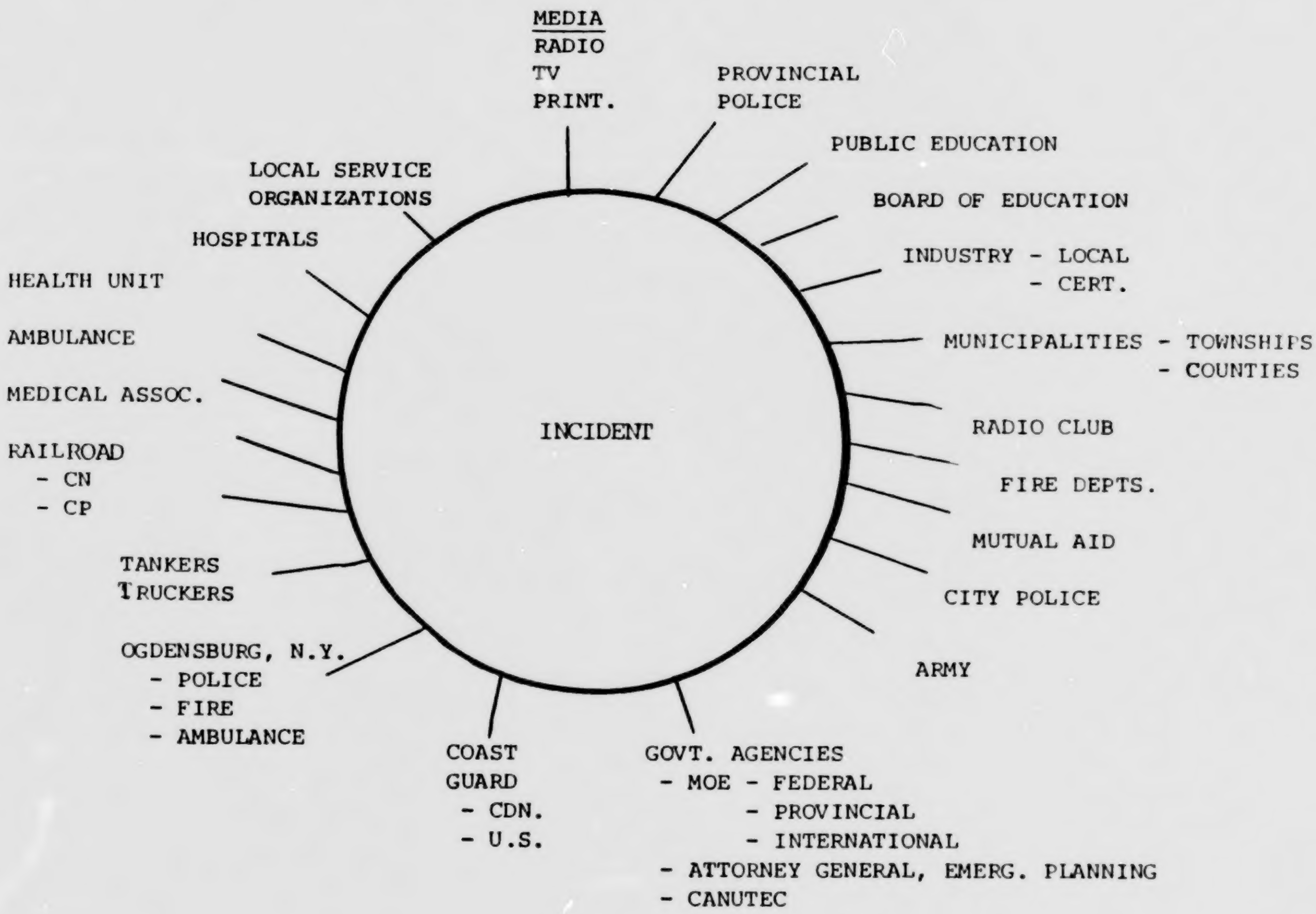
- o Open lines of communications.
- o Information sharing.
- o Coordinate emergency plans and procedures.
- o Interact with other emergency response agencies.
- o Joint education and training.
- o Common problem solving group.
- o Mutual aid assistance.

LOCAL GOVERNMENT RESPONSIBILITIES

1. Provide a safe community.
2. Assure the safety and well being of all residents and transients within community.
3. Establish public safety programs.
4. Protect lives, as well as private and public property.
5. Coordinate community emergency response forces during an emergency.
6. Develop plans and procedures to respond to emergencies.
7. Conduct training, drills, and exercises with other response agencies within the community, area, or state.

FIGURE 2

THE ELEMENTS OF INTEREST AROUND AN INCIDENT


MEDIA
RADIO
TV
PRINT.
PROVINCIAL POLICE
PUBLIC EDUCATION
BOARD OF EDUCATION
INDUSTRY - LOCAL
- CERT.
MUNICIPALITIES - TOWNSHIPS
- COUNTIES
RADIO CLUB
FIRE DEPTS.
MUTUAL AID
CITY POLICE
ARMY
GOVT. AGENCIES
- MOE - FEDERAL
- PROVINCIAL
- INTERNATIONAL
- ATTORNEY GENERAL, EMERG. PLANNING
- CANUTEC
COAST GUARD
- CDN.
- U.S.
OGDENSBURG, N.Y.
- POLICE
- FIRE
- AMBULANCE
TANKERS
TRUCKERS
RAILROAD
- CN
- CP
MEDICAL ASSOC.
AMBULANCE
HEALTH UNIT
HOSPITALS
LOCAL SERVICE ORGANIZATIONS
INCIDENT

OUR ACTUAL TEST INVOLVED A TANK TRAILER OF HCl (WATER AND SMOKE WERE USED) IN COLLISION WITH A SCHOOL BUS. ACID WAS LEAKING AND FUMING FROM THE TRAILER AND THERE WERE SERIOUS INJURIES TO THE BUS PASSENGERS. THE ACCIDENT OCCURRED AT THE BROCKVILLE CITY LIMITS SO AS TO INVOLVE THE BROCKVILLE FIRE DEPT. AND MUTUAL AID, THE BROCKVILLE POLICE AND THE ONTARIO PROVINCIAL POLICE.

THERE WERE THIRTY-FIVE STUDENT NURSES FROM ST. LAWRENCE COLLEGE ON THE BUS - THEY WERE DRESSED IN REALISTIC WOUNDS BY THE ONTARIO MINISTRY OF HEALTH PERSONNEL WITH INSTRUCTIONS ON HOW TO ACT. THIS WAS TO PROVIDE REALISM AND THE LARGE NUMBER WAS DESIRED BY THE TWO LOCAL HOSPITALS TO LOAD UP THE AMBULANCE SERVICES AND THE HOSPITAL EMERGENCY SYSTEMS.

THE TEST WAS A SUCCESS.

WE HAD EXCELLENT MEDIA COVERAGE ON LOCAL RADIO TALK SHOWS BEFORE THE EVENT, NEWSPAPER ARTICLES BEFORE AND AFTER AND LIVE RADIO COVERAGE.

THERE WAS COVERAGE BY THREE T.V. STATIONS. IN ADDITION DU PONT SPONSORED THE PRINTING OF 20,000 EDUCATIONAL BROCHURES THAT WERE INSERTED IN THE LOCAL NEWSPAPERS. THE PUBLIC WAS VERY RECEPTIVE TO THE TEST AND OVERALL IT WAS A VERY POSITIVE EXPERIENCE.

THE POST TEST RACK-UP IDENTIFIED MANY ITEMS INCLUDING THE FOLLOWING:

- STAFF CALL-IN PROCEDURES NEEDED UPDATING
- USE OF PHONES WAS A PROBLEM
- HCl IMPACT ON PATIENTS
- ADDITIONAL RUNNERS NEEDED
- PATIENT HANDLING NEEDED UPGRADING
- CLEAR CORRIDORS
- CAER GROUP IDENTIFICATION
- SUPPLIES FOR BURN VICTIMS - AVAILABLE FROM DU PONT
- LOSS OF PATIENT IN X-RAY
- PATIENT IDENTIFICATION
- HANDLING PRESS
- CHILD CARE DURING EMERGENCY
- NO PHONES AVAILABLE AT EMERGENCY CENTRE
- POOR COMMUNICATIONS BETWEEN AGENCIES
- NEED EXISTS TO HAVE AGENCIES WORK MORE CLOSELY
- OVERLOAD OF EXISTING TELEPHONE LINES

WE TEND TO THINK ONLY OF THE NEGATIVES. THERE WERE MANY BENEFITS FOR THE GROUPS INVOLVED AND FOR THE COMMUNITY. WHILE SOME OF THESE WERE UNDER CONSIDERATION, OUR CAER EFFORTS PROVIDED A TIMELY PUSH.

CAER - CHANGES IN THE COMMUNITY

LEEDS AND GRENVILLE	- $200,000 IMPROVEMENT IN THE MUTUAL AID RADIO SYSTEM - ALL TOWNSHIPS COMPLETING EMERGENCY PLANS AND A COORDINATED PLAN FOR THE UNITED COUNTIES BEING DEVELOPED
BROCKVILLE	- NEW DISPATCH PERSONNEL AND SYSTEM - HAZMET TEAM FORMED, LIONS CLUB DONATED TWO 'CHEMSUITS' - $3,000 ADDITIONAL IN BUDGET FOR EMERGENCY RESPONSE EDUCATION - UPGRADED EMERGENCY PLAN - NEW POLICE STATION APPROVED WITH UPGRADED EMERGENCY SPACE AND EQUIPMENT
PRESCOTT POLICE	- CENTRALIZED DISPATCH SYSTEM FOR ALL SERVICES PLUS THE ABILITY TO LINK INTO THE BROCKVILLE COMMUNICATIONS CENTRE AND SERVE AS A SECOND COMMAND CENTRE
BROCKVILLE OPP	- SCANNER, NEW PHONE LINES, DEDICATED PHONES, IDENTIFIED ALTERNATE HEADQUARTERS
GENERAL	- POLICE, FIRE, COAST GUARD, ARMY LINKAGE - POLITICANS AND OTHERS HAVE A BETTER UNDERSTANDING OF THEIR ROLES AND OF THE NEED TO BE PREPARED

DU PONT	- HAZARDOUS MATERIALS STUDY
	- AUDITING WAREHOUSES
	- AUDITING TRUCKERS
	- IMPROVED CERT
	- SAFER EMERG. SYSTEM COMPUTER FOR FUME MODELLING
	- COMMUNITY ACTIVITIES
	    - CERT IN FIRE PARADES
	    - CHEM ED '87
	    - NITROCHEM OPEN HOUSE
	    - 'ADOPT-A-SCHOOL'
	    - HELPING RIDEAU VALLEY HEALTH UNIT SET UP EMERGENCY COMM.
	    - OPEN HOUSE PLANNED FOR 1988-MAY
	    - ROUTINE TOURS OF SITE PLANNED

THE BENEFITS HAVE BEEN SUCH THAT THERE HAS BEEN STRONG SUPPORT FOR THE COMMITTEE TO CONTINUE.

WE MET TEN TIMES IN 1987 AND COMPLETED A COMMUNICATIONS TEST IN NOVEMBER. THIS INVOLVED THE SIMULATION OF A LARGE CL_2 RELEASE FROM OUR PLANT OF SUCH MAGNITUDE THAT THE FIRST RESPONDERS COULDN'T HANDLE AND REQUESTED THE ESTABLISHMENT OF CONTROL GROUPS IN AUGUSTA TOWNSHIP AND IN OGDENSBURG, N.Y. WE USED THE SERVICES OF EMERGENCY PLANNING ONTARIO FOR THE EXERCISE DETAILS. WE MODELED THE RELEASE ON OUR SAFER EMERGENCY SYSTEM TO PROVIDE A REAL ON-LINE SITUATION FOR THE TEST.

THE VARIOUS GROUPS INVOLVED WERE PLEASED WITH THE TEST AND WILL INCORPORATE THE LEARNINGS TO FURTHER ENHANCE THEIR PREPAREDNESS FOR EMERGENCIES. AGAIN, THE MAJOR LEARNINGS WERE IN THE COMMUNICATION AREA WITH SPECIAL EMPHASIS ON THE AVAILABILITY OF ADQUATE RADIO FACILITIES AND LINE LOAD CONTROL ON THE TELEPHONE SYSTEM.

WE ARE ALREADY PLANNING 1988 ACTIVITIES WHICH WILL INCLUDE A COMMUNICATION TEST IN MAY AND A PHYSICAL TEST IN AUGUST. DU PONT IS SPONSORING A THREE DAY HAZMAT TRAINING SEMINAR IN THE FALL FOR OUR CERT TEAM AND EMERGENCY PERSONNEL FROM BOTH SIDES OF THE BORDER WILL BE INCLUDED AS WELL.

CAER IS ALIVE AND WELL IN OUR AREA AND WHILE IT INVOLVES A MASSIVE COMMUNICATIONS EFFORT, IS UNDOUBTEDLY WORTHWHILE. WORTHWHILE FROM EMERGENCY PLANNING BUT ALSO COMMUNITY RELATIONS AND UNDERSTANDING AS WE WORK TO IMPROVE THE PERCEPTIONS OF THE CHEMICAL INUSTRY.

WHILE OUR GROUP IS A SMALL VOICE IN THE WILDERNESS THE OVERWHELMING NEED IS THERE AND I HOPE EACH OF YOU WILL GRASP THIS WONDERFUL TOOL AND OPPORTUNITY TO HELP THE PUBLIC, OUR COMMUNITY AND OUR INDUSTRY.

ZONING TO PROTECT THE PUBLIC

Peter Robb
Dow Chemical Canada Inc.

How often have you driven past a chemical company and thought of what it would be like to live right next door? You'd probably wonder what systems were in place to protect you in case of a major incident. You might also wonder what constitutes a safe distance between your home and the plant site.

As the site manager at Dow Chemical Canada in Varennes, just south of Montreal, I have wondered about these issues too. Dow is a member of the Varennes Industrial Association -- called VIA for short. One of VIA's highest priorities is to establish a buffer zone between our plants and the residential area around us. We want to protect the people with whom we share the community.

Buffer zones, like the one we have in mind at Varennes, should be a part of every community where chemicals are produced. Because, despite our use of high technology and precautionary measures, there still exists the potential for accidents. Together, we must establish plans to protect the community against this.

Those people who work for chemical producers or other related associations should consider talking to their municipal leaders about establishing buffer zones if they don't already exist. Protecting the well-being of the people in the communities that surround us is our first responsibility. It is also a key element of the chemical industry's commitment to Responsible Care.

Those who are regulators should consider recommending that buffer zones be established in existing plant locations and around new sites.

What follows is an analysis of the importance of municipal zoning, followed by an examination of the VIA buffer zone study based on dispersion modelling.

THE IMPORTANCE OF ZONING

There are two fundamental reasons for establishing a buffer zone between industry and residential areas.

First, despite the care that the chemical industry takes, there are still some inconveniences associated with our presence. These inconveniences vary from the glare of bright lights to the noise of transport trucks. A buffer zone would provide a cushion of distance to dim the glare and muffle the noises.

Second, the volatile nature of the chemicals we produce means that there is a potential for a major incident. The Bhopal event of December 1984 was a lesson for chemical producers around the world. It was a very real example of what can happen without a buffer zone between a chemical manufacturing site and a community.

When that release of methyl isocyanate occurred, a warning siren sounded but people didn't know what it meant or how to respond. Nearly

3000 people living in shacks next to the chemical plant died and many others were injured.

We must ensure that a similar incident could never happen in our plant communities here in Canada.

Since Bhopal, a movement has grown here in North America to educate and train the people about the risks involved in the manufacture of chemicals and how we are managing those risks.

The members of the Canadian Chemical Producers Association (CCPA) have endorsed a program called CAER (Community Awareness and Emergency Response). CAER involves many outreach programs which vary from company to company. These programs centre on respect for the needs of community members. At the Varennes Industrial Association, CAER prompted us to look at what we could do for the Varennes community.

BUFFER ZONE STUDY

At the invitation of the city planner, the member companies of VIA submitted a report to the City Council which examined what the effects would be in the event of a major chemical disaster. The report, submitted in October of 1987, dramatically demonstrated the need to zone the area to protect the public.

Background

The first chemical company came to Varennes in 1952. Now there are nine companies. In 35 years, the residential area has grown to such an extent that today there is only a zone of 600 metres between it and industry.

To further complicate matters, the city of Varennes introduced a new law in 1986 to relax this protective zone.
All nine chemical companies are members of VIA and as a group stand firmly against this. We feel that it would jeopardize the safety of the community in the northeast corner of the city.

No one plans on having a major chemical accident. But we can't ignore that the potential for an accident exists. Each company works diligently to minimize that potential. All our facilities are equipped with protection systems. We have employees who are specially trained to contain minor incidents before they become major ones and we have emergency procedures that go into effect as soon as an alarm is sounded.

However, we still feel that a buffer zone would go one step further in the protection of the community.

First, a buffer zone would help minimize the effects of the nuisance factors associated with living close to a chemical plant.

Despite our continued efforts to improve technology and comply with the stiffer regulations introduced by government, there are still some nuisances. They do not pose a health threat.

These include: the appearance of plants, noise, dust, odors, smoke, vibrations, heat, and glare from lights. Also, there is the intermittent or continuing presence of chemicals which can modify the air quality of the residential zone. Even though these nuisances don't constitute a danger to the community they can affect the quality of life.

Secondly, we believe that a buffer zone should be in place in the event of a major disaster, such as a fire, a spill, a gas cloud, or an explosion. To demonstrate how vital this is, VIA conducted a buffer zone study.

Six of the chemical companies located in Varennes looked at their most potentially dangerous product and predicted what would happen if it was to be released into the environment. The possibilities included the release of toxic chemicals to the air or an explosion involving flammable products.

Using dispersion modelling, we calculated the effects of loss of containment for each product under the worst possible conditions. These conditions included the failure of all back-up systems in the plant -- both equipment and procedures. Something that is almost beyond the realm of probability.

The dispersion modelling took into account many factors:

- quantity released, including source strength;
- the physical properties of the chemical substance;
- nature of the release;
- the storage conditions;
- the rate of evaporation;
- the wind velocity;
- the wind direction;
- the atmospheric pressure;
- the relative humidity;
- the ambient temperature;
- the solar radiation;
- the topography of the surrounding terrain;
- and the spill area (if liquid).

The number of factors involved can make it difficult to determine exactly what can happen. This is where dispersion modelling programs come in.

There are many different dispersion modelling programs available on the market. They are based on different coefficients of dispersion such as those developed by Pasquill-Gifford, Slade and others. The selection of an appropriate program depends on all of the factors listed in the last paragraph.

In the VIA case, dispersion modelling clearly demonstrated that, despite precautions and inspections, a major incident could put the well-being of the community in danger.

DISPERSION MODELLING

The use of dispersion modelling is an effective way to determine appropriate zones to protect that well-being. The positive results of the VIA study may encourage others in the industry to use it to determine their own buffer zones.

It is important to emphasize that each of the Varennes scenarios are estimates of what could happen in the worst case. It is unlikely that any of these situations will ever arise.

To make it true to our situation however, some aspects of the worst case scenarios were arbitrarily chosen, such as the velocity of the prevailing winds. We used this, and other information, to calculate the affected area around the plants for each scenario.

These scenarios were divided by the type of chemicals involved. (Table 1) For example, we looked at toxic products at each plant. In all three cases, the concentrations given show how far the Immediately Dangerous to Life and Health (IDLH) zone will extend from the source location under the given conditions.

Table 1

CHARACTERISTICS OF THE HYPOTHETICAL DANGER ZONE FOR EACH OF THE VIA MEMBER PLANTS

Plant	Chemical product	Danger radius (metres)	Concentration, at the periphery of the zone (parts per million)
Alcools de Commerce	Benzene Ethylene	201 1,320	2,000 27,000
Dow	Butadiene	768	20,000
ERCO	Ammonia	829	500
Himont	Propylene	232	20,000
Hoechst	Vinyl acetate	34	26,000
NL Chem	Chlorine	240	25
Pétromont	Propylene	650	20,000

We also looked at flammable products and the mimimum concentration required for a fire or explosion to occur if the gas ccame into contact with an energy source. This is known as the Lower Flammable Limit or LFL.

Overall, the information for each product was plotted onto a map which indicated the circles of danger around the respective plants. (Figure 1) This map shows what we believe could happen in the worst case.

It is unlikely, however, that these kinds of major incidents could ever happen. We have built our plants and trained our people with safety as our priority. We have sophisticated equipment that constantly monitors the quality of the air around us. And we hold dry runs on a regular basis to test our emergency preparedness.

RECOMMENDATIONS

The Varennes Buffer Zone study accomplished two things. First, it resulted in a number of changes to procedures, particularly in the manufacture and transportation of chemicals by VIA member companies.

And second, we were able to recommend to the city of Varennes that a buffer zone be established that would accomodate the circles of danger. This recommended zone is roughly in the shape of a banana at the northeast corner of the city and is referred to as the "Banana Zone" (Figure 2). VIA recommended that residential development in this zone never be allowed.

VIA also recommended that the city study the possibility of building a physical barrier around the perimeter of this zone. Made of trees and landscaped hills, the barrier would help to solve some of the nuisances associated with the industry presence. For example, the barrier would obscure the view of the plants, and it would diminish the noise levels and prevent heavier gas clouds from getting into the residential area.

And finally, VIA recommended that the city redefine the industrial zone to take into consideration existing industries and provide for future industrial expansion (Figure 3). This redefined zone would allow industry to grow without affecting the residential area.

CONCLUSION

As people involved in the chemical industry, we have the opportunity to prevent major chemical incidents. By establishing buffer zones between industrial and residential areas we can maximize the protection of the people who live near our chemical plants. The use of dispersion modelling is an excellent method of determining where those buffer zones should be.

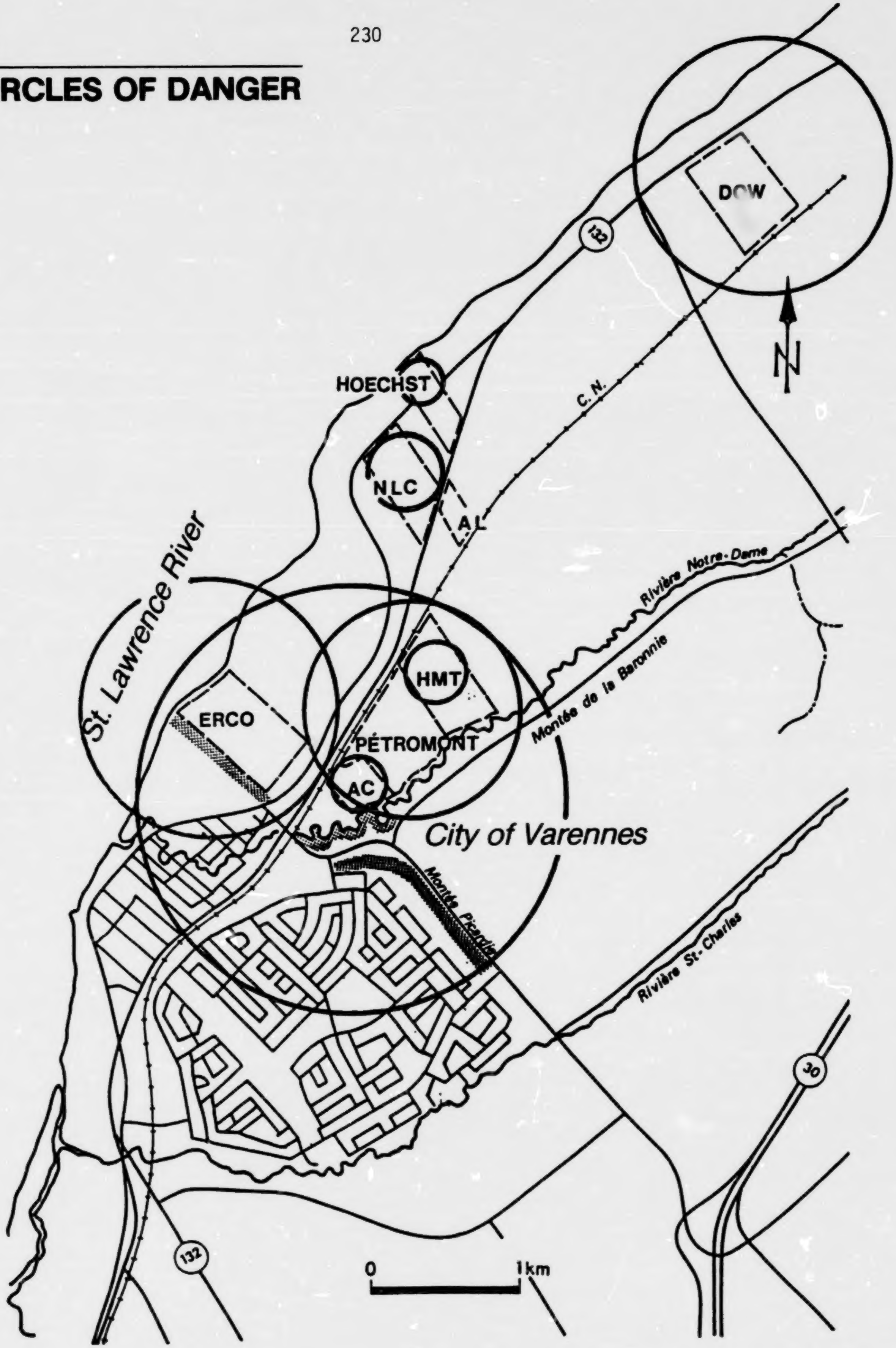
The Varennes Industrial Association's Buffer Zone Study demonstrated that for at least one city, there is a need for a buffer between our industry and the community. Our use of dispersion modelling helped us to determine that the industrial sector and the residential sector are too close to one another.

Not only would a buffer zone protect residents from potential incidents, it would also help to reduce the nuisance factors associated with our industry.

The next step for us is an obvious one -- we need to work with the city of Varennes to reinstate an adequate buffer. This would protect

Figure 1

THE CIRCLES OF DANGER


DOW
132
N
HOECHST
C.N.
NLC
A.L.
St. Lawrence River
Rivière Notre-Dame
Montée de la Baronnie
HMT
ERCO
PÉTROMONT
AC
City of Varennes
Montée Picardie
Rivière St-Charles
30
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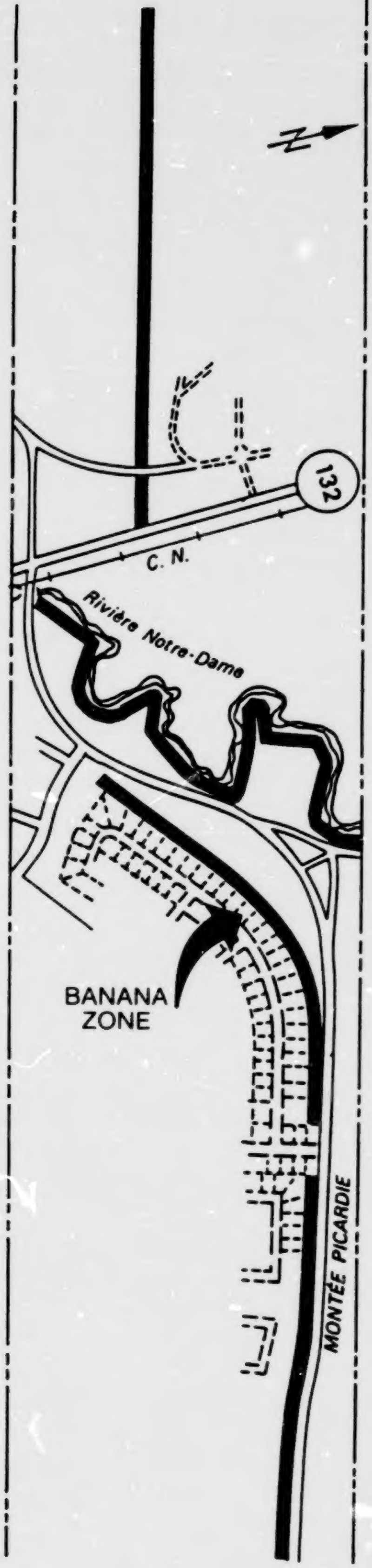
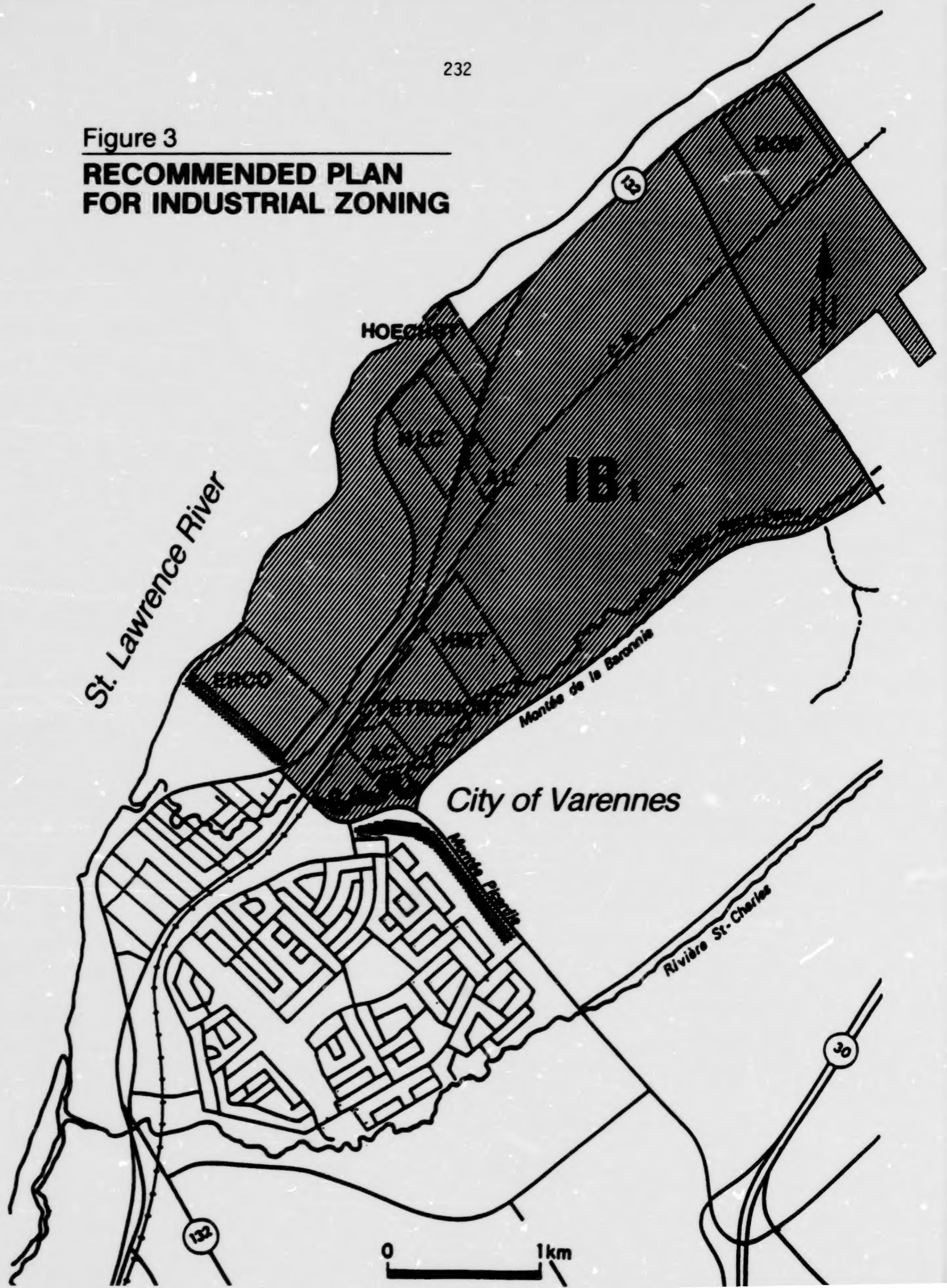

132
C. N.
Rivière Notre-Dame
BANANA ZONE
MONTÉE PICARDIE

Figure 2

PROPOSED CONCEPT
by Philippe Grimard

Figure 3

RECOMMENDED PLAN FOR INDUSTRIAL ZONING



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HOECHST
NLC
IB₁
St. Lawrence River
ERCO
PETROMONT
Montée de la Baronnie
City of Varennes
Montée Picardie
Rivière St-Charles
30
132
0
1km

future as well as current residents of the city. It would also reinforce our commitment to the communities in which we operate.

The VIA study is one that can have universal application. If you are a member of the chemical industry, it can relate to your own situation.

As our Responsible Care commitment emphasizes, we have a responsibility to protect those who trust us enough to live right next door.

MIACC

MAJOR INDUSTRIAL ACCIDENTS COORDINATING COMMITTEE

BY

R. MORCOS AND D.W. BISSETT

ENVIRONMENT CANADA

THANK YOU MR. CHAIRMAN FOR GIVING ME THE OPPORTUNITY TO ADDRESS THIS SEMINAR AND TALK ABOUT MIACC - THE MAJOR INDUSTRIAL ACCIDENTS COORDINATING COMMITTEE .

ALLOW ME TO PRESENT A BRIEF HISTORICAL OF THIS ACTIVITY AND BRING YOU UP-TO-DATE ON WHERE WE ARE NOW AND WHAT WE EXPECT TO DO IN THE FUTURE, IN CONCERT WITH THE INDUSTRY AND ALL LEVEL OF GOVERNMENTS, REGARDING ACCIDENTS INVOLVING DANGEROUS SUBSTANCES.

THE TRAGIC ACCIDENT OF BHOPAL TRIGGERED THE FORMATION OF AN INDUSTRY/ GOVERNMENT TASK FORCE TO SPECIFICALLY EXAMINE THE SITUATION IN CANADA IN REGARD TO THE POTENTIAL FOR ACCIDENTS, THE EXISTING PREVENTIVE AND RESPONSE MEASURES AND THEIR ADEQUACY.

THIS TASK FORCE PUBLISHED ITS FINDINGS IN A REPORT ENTITLED: "BHOPAL AFTERMATH REVIEW: AN ASSESSMENT OF THE CANADIAN SITUATION". I HOPE THAT ALL OF YOU HAVE SEEN THIS REPORT AND IF NOT WE STILL HAVE COPIES AVAILABLE. IN THIS REPORT THE TASK FORCE PRESENTED 21 RECOMMENDATIONS RELATED TO ACCIDENT PREVENTION AND RESPONSE, COVERING A MULTITUDE OF AREAS, SUCH AS:

> RISK ASSESSMENT, SAFETY AUDITS, LESSONS FROM NEAR MISSES, TRAINING OF 1ST RESPONDERS, CAER, AVAILABILITY OF MEDICAL INFORMATION,..

THE REPORT WAS WIDELY DISTRIBUTED, ESPECIALLY THROUGH INDUSTRIAL ASSOCIATIONS SUCH AS PACE AND CCPA. BEFORE FINALIZING THIS REPORT, 700 COPIES OF THE DRAFT VERSION WERE DISTRIBUTED FOR COMMENTS AND SIX PUBLIC MEETINGS WERE HELD ACROSS CANADA. THE COMMENT WE KEPT HEARING IS THE NEED OF AN ORGANIZED FOLLOW-UP TO COORDINATE THE IMPLEMENTATION OF THE RECOMMENDATIONS.

WHEN THE REPORT WAS RELEASED JOINTLY BY THE MINISTER OF THE ENVIRONMENT AND THE MINISTER RESPONSIBLE FOR EMERGENCY PREPAREDNESS CANADA, BOTH INDICATED THE NEED TO FOLLOW-UP ON THE IMPLEMENTATION OF THE REPORT'S RECOMMENDATIONS.

CCPA'S PRESIDENT MADE A PUBLIC STATEMENT, THE DAY FOLLOWING THE RELEASE OF THE REPORT, INDICATING CCPA'S INTENTION TO COOPERATE WITH THE GOVERNMENT TO IMPLEMENT THE RECOMMENDATIONS.

THESE THREE ORGANIZATIONS WERE THE NUCLEUS OF THE INTERIM STEERING COMMITTEE FOR THE " MAJOR INDUSTRIAL ACCIDENTS COORDINATING COMMITTEE (MIACC)". THIS COMMITTEE WAS STRUCK TO COORDINATE THE IMPLEMENTATION OF THE BHOPAL REPORT RECOMMENDATIONS. THIS NUCLEUS SOON GREW TO INCLUDE 8 ORGANIZATIONS:

> EPC, ENVIRONMENT CANADA, TRANSPORT CANADA, ALBERTA PUBLIC SAFETY SERVICES, BUREAU DE LA PROTECTION CIVILE DU QUEBEC, SASKATCHEWAN EMERGENCY MEASURES ORGANIZATION, CCPA AND PACE.

THE ORGANIZING COMMITTEE FELT THE NEED OF INPUT FROM A LARGE CROSS SECTION AND INVITED MANY PERSONS AND ORGANIZATIONS TO THE FIRST MIACC CONFERENCE WHICH WAS HELD ON NOVEMBER 19 AND 20, 1987. THE CONFERENCE WAS ATTENDED BY MORE THAN 70 PERSONS FROM ACROSS CANADA, REPRESENTING GOVERNMENTS, INDUSTRIAL AND PROFESSIONAL ASSOCIATIONS (SUCH AS THE CANADIAN MEDICAL ASSOCIATION, THE CANADIAN ASSOCIATION OF CHIEFS OF POLICE,ETC.) AS WELL AS A PUBLIC INTEREST GROUP.

A CONSULTANT WAS HIRED TO HELP THE ORGANIZING COMMITTEE TO ESTABLISH CONTACTS AND ACT AS A MODERATOR FOR THE CONFERENCE AT THE PLENARY SESSIONS. FOUR WORKSHOPS WERE ANIMATED BY PROFESSIONALS FROM GOVERNMENT AND INDUSTRY AND DISCUSSED THE NEED FOR MIACC AND THE PROPOSED OBJECTIVE AND TERMS OF REFERENCE. THE NEXT DAY, RAPPORTEURS FROM EACH WORKSHOP PRESENTED THE RECOMMENDATIONS OF THAT WORKSHOP AT A PLENARY SESSION. IN SUMMARY, THE ATTENDEES INDICATED A VERY STRONG SUPPORT FOR THE MIACC CONCEPT AND RECOMMENDED SOME MINOR CHANGES TO THE WORDING OF THE PROPOSED OBJECTIVE AND TERMS OF REFERENCE.

THE CONFERENCE AGREED ON THE NEED FOR A STEERING COMMITTEEE TO IMPLEMENT THE TERMS OF REFERENCE. THIS WILL HAVE REPRESENTATION FROM THE THREE LEVELS OF GOVERNMENT, INDUSTRIAL AND PROFESSIONAL ASSOCIATIONS, RESEARCH AND PUBLIC INTEREST GROUPS (ATTACH.2).

THE STEERING COMMITTEE, AT ITS MEETING OF JANUARY 5, 1988 TOOK INTO CONSIDERATION THE COMMENTS RECEIVED DURING THE CONFERENCE. THE FINAL VERSION IS SHOWN IN (ATTACHMENT # 1).

MIACC'S OBJECTIVE IS TO PROVIDE A FOCUS FOR ACTIONS AND LEADERSHIP TO REDUCE THE NUMBER AND IMPACT OF MAJOR ACCIDENTS INVOLVING DANGEROUS SUBSTANCES ON PUBLIC SAFETY, HEALTH AND THE ENVIRONMENT BY IMPROVING PREVENTION, PREPAREDNESS AND RESPONSE MEASSURES. THIS OBJECTIVE WILL BE ACHIEVED THROUGH THE IMPLEMENTATION OF THE TERMS OF REFERENCE SHOWN HERE:

1- **MIACC WILL REVIEW ACTIVITIES AND PROMOTE STRATEGIES AND RESEARCH..**

2- **MIACC WILL HAVE A COORDINATING ROLE AMONGST INTERESTED GROUPS**

3- **MIACC WILL PROVIDE A FORUM FOR INFORMATION EXCHANGE..**

4- **MIACC WILL ESTABLISH AND MAINTAIN AN INVENTORY OF EXISTING AND PLANNED ACTIVITIES RELATED TO ACHIEVING THE OBJECTIVE.**

TO BE ABLE TO CARRY OUT TERM OF REFERENCE # 1,2 & 3 MIACC WILL ESTABLISH AND MAINTAIN AN INVENTORY (T.O.R. # 4). THIS INVENTORY HAS BEEN STARTED BY ASKING PERSONS AND ORGANIZATIONS TO COMMUNICATE THEIR ACTIVITIES AND PROGRAMS RELATED TO THE BHOPAL REVIEW REPORT RECOMMENDATIONS TO THE STEERING COMMITTEE THROUGH THE " INPUT TO FOLLOW-UP REPORT" WHICH WAS DISTRIBUTED AT THE NOVEMBER CONFERENCE. ANY PERSON INTERESTED IN THIS, PLEASE CONTACT ME. AT THIS STAGE, SOME ORGANIZATIONS HAVE COMMUNICATED THEIR PROGRAMS, FOR EACH OF THE 21 RECOMMENDATIONS, AND THESE HAVE BEEN INPUTED IN THE INVENTORY, IN A VERY BRIEF FORMAT (PLEASE REFER TO ATTACHMENT # 3). WHEN MORE DETAIL INFORMATION IS NECESSARY, IT WILL BE INCLUDED IN THE APPENDIX (PLEASE REFER TO ATTACHMENT # 4).

THE MORE INPUT WE RECEIVE ON THIS ITEM, THE MORE COMPLETE DATA BASE THE STEERING COMMITTEE WILL HAVE AT ITS DISPOSITION FOR REVIEW AND FORMULATION OF RECOMMENDATIONS AND PLAN OF ACTIONS TO FILL THE GAPS. THIS INVENTORY CAN ALSO BE USED AS A COMMUNICATION AND INFORMATION TOOL BY DIFFERENT AGENCIES.

THE FIRST TERM OF REFERENCE INDICATES THAT MIACC WILL SUPPORT AND PROMOTE STRATEGIES TO ACHIEVE THE OBJECTIVE. IN OTHER WORDS IT WILL NOT BE INVOLVED IN AN OPERATIONAL ROLE, BUT WILL ENCOURAGE THE PARTIES INVOLVED TO CARRY OUT THE NECESSARY ACTIVITIES TO ACHIEVE THE OBJECTIVE.

HOWEVER INDIVIDUAL MEMBERS OF MIACC, BECAUSE OF THEIR RESPONSIBILITIES, WILL CARRY OUT SPECIFIC PROGRAMS; FOR EXAMPLE, MUNICIPALITIES MAY REGULATE AND MAINTAIN BUFFER ZONES OR DESIGNATE DANGEROUS GOODS ROUTES. INDUSTRIAL PLANTS WILL CONTINUE TO KEEP THE COMMUNITY INFORMED THROUGH THEIR COMMUNITY AWARENESS / EMERGENCY RESPONSE PROGRAMS (CAER), TRAINING TO FIRST RESPONDERS WILL BE DISCUSSED IN A SEPARATE PAPER.

MIACC WILL HAVE A COORDINATING ROLE AMONGST INTERESTED PARTIES, FOR EXAMPLE BY MAINTAINING INVENTORIES OF ACTIONS AND MAKING THEM AVAILABLE, THIS COULD PREVENT DUPLICATION OF EFFORTS AND RESOURCES.

MIACC WILL PROVIDE A FORUM FOR INFORMATION EXCHANGE (THROUGH NEWS LETTERS,..) ON PROGRAMS AND ACTIVITIES RELATED TO INDUSTRIAL ACCIDENTS. THE INFORMATION EXCHANGE WILL BE

ENCOURAGED AND SUPPORTED. BETTER COMMUNICATIONS AND ACCESS TO INFORMATION THROUGH CONTACT AND NEWSLETTERS WILL FACILITATE MANY TASKS AND SAVE RESOURCES.

THE STEERING COMMITTEE WILL PUBLISH A REGULAR NEWSLETTER WHICH WILL BE SENT TO MIACC MEMBERS AND TO ALL INTERESTED PARTIES TO KEEP THEM INFORMED OF THE ACTIVITIES WHICH THE STEERING COMMITTEE IS CARRYING OUT ON THEIR BEHALF AND TO CONVEY MATERIAL AND INFORMATION PERTINENT TO THIS ACTIVITY. IF YOU WOULD LIKE TO BE ON THE MAILING LIST, PLEASE LEAVE WITH ME YOUR BUSINESS CARD BEFORE THE END OF THE SEMINAR.

OTHER COUNTRIES ARE TAKING STEPS TO REDUCE THE NUMBER AND IMPACT OF MAJOR ACCIDENTS INVOLVING DANGEROUS SUBSTANCES; CANADA IS INVOLVED IN THE OECD PROGRAM RELATED TO ACCIDENTS INVOLVING HAZARDOUS SUBSTANCES AND OUR REPRESENTATIVES ARE IN PARIS THIS WEEK TO AGREE ON BEHALF OF CANADA TO TWO DECISIONS WHICH WILL BE A REQUIREMENT FOR ALL MEMBER COUNTRIES. THESE TWO DECISIONS ARE IN RESPECT OF:

I) PROVISION OF INFORMATION TO THE PUBLIC AND PUBLIC PARTICIPATION IN DECISION MAKING, AND
II) TRANSFRONTIER EXCHANGE OF INFORMATION .

WE BELIEVE THAT THE MIACC INITIATIVE IS UNIQUE IN THAT IT DOES NOT INVOLVE A STRICTLY REGULATORY APPROACH AS MOST OTHER COUNTRIES HAVE ADOPTED. RATHER, IT INVOLVES A COOPERATIVE EFFORT FROM ALL LEVELS OF GOVERNMENT AND INDUSTRY TO REDUCE THE RISK OF CHEMICAL ACCIDENTS AND IMPROVE OUR SITUATION IN TERMS OF ACCIDENT PREVENTION, THE STATE OF PREPAREDNESS AND RESPONSE COUNTERMEASURES.

FOR THIS REASON, MANY COUNTRIES ARE OBSERVING THIS CANADIAN EXPERIENCE, THE WAY IT IS CONCEIVED AND IMPLEMENTED AND ITS RESULTS. THE STEERING COMMITTEE FEELS STRONGLY THAT THIS INITIATIVE CAN BE A SUCCESS WITH THE COLLABORATION OF ALL THE PARTIES INVOLVED, BE IT GOVERNMENT AGENCIES, INDUSTRIES, SMALL AND LARGE, PROFESSIONAL AND INDUSTRIAL ASSOCIATIONS, UNIVERSITIES AND PUBLIC INTEREST GROUPS.

IN CONCLUSION, I WOULD LIKE TO SAY THAT MANY INDUSTRIES AND GOVERNMENTS HAVE TAKEN POSITIVE STEPS TOWARDS ACCIDENT PREVENTION AND RESPONSE.

LAST SUMMER, THE ONTARIO GOVERNMENT INTRODUCED AND PASSED AMENDMENTS TO THE "OCCUPATIONAL HEALTH AND SAFETY ACT" WHICH INCLUDES REQUIREMENTS MAKING MSDS AVAILABLE TO WORKERS, MEDICAL OFFICERS OF HEALTH AND FIRE DEPARTMENTS AS WELL AS CARRYING OUT RISK ASSESSMENTS AND MAKING THE RESULTS AVAILABLE TO WORKERS.

IN NOVA SCOTIA, A MINISTER OF ENVIRONMENT'S TASK FORCE ON HAZARDOUS WASTE MANAGEMENT PRESENTED 51 RECOMMENDATIONS, ESPECIALLY RE: FILING OF INVENTORIES, REPORTING SPILLS AND

EVALUATING EMERGENCY RESPONSE,.. THE GOVERNMENT IS COMMITTED TO IMPLEMENTING ALL 51 RECOMMENDATIONS.

ALBERTA IS ALSO EVALUATING ITS OPTIONS AND MAY REQUIRE THAT ALL SITES FILE AN EMERGENCY RESPONSE PLAN.

AND FINALLY I WOULD LIKE TO LEAVE YOU WITH THIS: THE 2 KEY ACTIONS REQUIRED ARE :

- THE NEED TO ESTABLISH AND /OR IMPROVE ACCIDENT PREVENTION PROCEDURES,
- THE IMPORTANCE OF PROGRAMS LIKE CAER (COMMUNITY AWARENESS/ EMERGENCY RESPONSE).

I THANK YOU FOR YOUR ATTENTION, IF THERE ARE ANY QUESTIONS I WILL TRY MY BEST TO ANSWER THEM

THANK YOU.

Att # 1

MAJOR INDUSTRIAL ACCIDENTS
COORDINATING COMMITTEE
MIACC

OBJECTIVE

TO PROVIDE, FOR ALL INTERESTED PARTIES, A FOCUS FOR ACTIONS AND LEADERSHIP TO REDUCE MAJOR ACCIDENTS INVOLVING DANGEROUS SUBSTANCES IN TERMS OF NUMBER AND SEVERITY AS THEY IMPACT ON PUBLIC SAFETY, HEALTH AND THE ENVIRONMENT, BY IMPROVING PREVENTION PREPAREDNESS AND RESPONSE PROGRAMS.

TERMS OF REFERENCE

1. MIACC WILL REVIEW ACTIVITIES AND PROMOTE STRATEGIES AND RESEARCH BY ACTIVELY SEEKING COMMITMENT FROM ALL PARTICIPANTS AND BY MONITORING PROGRESS TOWARDS THE ACHIEVEMENT OF THE OBJECTIVE.

2. MIACC WILL HAVE A COORDINATING ROLE AMONGST INTERESTED GROUPS.

3. MIACC WILL PROVIDE A FORUM FOR INFORMATION EXCHANGE ON PROGRAMS AND ACTIVITIES RELATED TO MAJOR ACCIDENTS THROUGH NEWSLETTERS AND OTHER COMMUNICATIONS.

4. MIACC WILL ESTABLISH AND MAINTAIN AN INVENTORY OF EXISTING AND PLANNED ACTIVITIES RELATED TO ACHIEVING THE OBJECTIVE.

JAN 5, 1988
AS ADOPTED BY THE STEERING COMMITTEE

Att.# 2

M I A C C

STEERING COMMITTEE MEMBERS

	Name	**Telephone**	**Agency**	**DEX**
*	E.L. Shipley	613-992-2727	EMERGENCY PREPAREDNESS CANADA	613-996-1901
s	G. Riley	613-992-7073	EMERGENCY PREPAREDNESS CANADA	
s	L. Swick	613-993-6890	EMERGENCY PREPAREDNESS CANADA	
*	P.M. Higgins	819-997-1298	ENVIRONMENT CANADA	819-997-0547
s	D.W. Bissett	819-953-1131	ENVIRONMENT CANADA	
s	R. Morcos	819-953-1137	ENVIRONMENT CANADA	
*	J. Read	613-998-1147	TRANSPORT CANADA	613-952-1338
s	M. Salib	613-990-1132	TRANSPORT CANADA	
s	R. Simard	613-998-4187	TRANSPORT CANADA	
	P. Brien	418-643-3256	BUREAU DE LA PROTECTION CIVILE DU QUEBEC	418-643-1941
	M. Hegan	306-787-9563	SASKATCHEWAN EMERGENCY MEASURES ORGANIZATION	306-359-0427
	M. Egener	403-451-7107	ALBERTA PUBLIC SAFETY SERVICES	403-451-7199
	D.N. Cassidy	613-233-1106	CANADIAN ASSOCIATION OF CHIEFS OF POLICE	
	E.Therien	613-749-3825	CANADIAN ASSOCIATION OF FIRE CHIEFS	
	C. Johnson	519-736-2111	CANADIAN CHEMICAL PRODUCERS' ASSOCIATION	519-736-5131
	J. Dillon	613-233-8423	CANADIAN MANUFACTURERS' ASSOCIATION	613-233-6048
	L.P. Tardif	613-236-9426	CANADIAN TRUCKING ASSOCIATION	613-563-2701
	S. Tom	613-236-9426	FEDERATION OF CANADIAN MUNICIPALITIES	
	J. Shortreed	519-885-1211	-3377 INSTITUTE FOR RISK RESEARCH	519-888-4521
	J. Reed	416-441-7673	PETROLEUM ASSOCIATION FOR THE CONSERVATION OF THE CANADIAN ENVIRONMENT	416-441-7700

* Co-Chairman
s Secretariat

December 23, 1987

Att # 3

Chemical Incident Simulation Exercises

Conclusion 15

While many municipalities across Canada have emergency plans to respond to major incidents, very few emergency organizations hold simulation exercises to test the adequacy of their plans. The Chemical Valley Emergency Control Organization in Sarnia and FORT MAP (the mutual aid response organization in Fort Saskatchewan) both hold annual simulations; their programs could be used as models for other emergency organizations.

Recommendation 15

To ensure the adequacy of emergency response plans, all emergency organizations should periodically carry out exercises to simulate an incident, evaluate the effectiveness of the response and make improvements where necessary. (Federal: E, P, T; Provincial: E, P; Municipalities; Industry)

EXAMPLE OF INPUT TO FOLLOW-UP REPORT

R	AGENCIES		PROV	PROGRAMS	S	CONTACT	TELEPHONE
15)							
	NB EMO		NB	Mock disaster exercises, frequently	E		506-453-2133
	BPCQ, HydroQuebec	Gentilly,	Qué	Operation DERAD 1: 1985/DERAD 2	E,P		
		Beauharnois,	Qué	Exercise: Mar 1987	E		
	Ultramar		Qué	Exer : 1986	E		
	Shell		Qué	Exer : 1987	E		
	APQ:		Qué	Simulation: min 6 exercices/year (appendix 15)	E	G.Archambault	418-875-4340
	Sept-Iles			Exer : Oct 86, Sept 87	E		
	Québec			Exer : Sep 86, & to be determined	P		
	Rimouski			Exer : Jun 86, Sep 87	E		
	Montréal			Exer : Oct 86, Sep 87	E		
	Chicoutimi			Exer : May 86, Sep 87	E		
	Abitibi			Exer : Aug 86, Sept 87	P		
	Emergency planning Ontario		Ont	Exercise & assistance available to all municip.	E	J.L. Ellard	416-965-6708
	DuPont	Maitland,	Ont	Exercise: Nov.20,1986	E	John Meyers	
	Uniroyal Chemical	Elmira,	Ont	Exercise	E	Walter Ruck	
	Union Carbide	Moore Twp,	Ont	Exercise: July 86	E	R. Lawton	
	Manitoba Environment		MA	Environmental Accident Response & Exercise	E	Dave Ediger	204-945-7042
	Manitoba EMO		MA	Training & Education	E	L. Gwiazda	204-945-4792
	Union Carbide	Prentiss,	AB	Exercise	E	Robert Seath	
	Alberta Gas Ethylene		AB	Exer	E	W. Stephenson	
	APSS		AB	Exer with Municipalities, Sour Gas Release Plan	E	R. Willhauk	403-451-7119
	APSS		AB	is exercised annually, real emergencies enable			
	APSS		AB	evaluation/improvement of ERP			
	Dept Munic Affairs (Emerg Services)		NWT	Exercises (territ, Municip, reg)	E		403-673-7554
	Dept Justice (Mining Inspection Serv)		NWT	Training & Rescue exercises for mine rescue crews	E		

R: RECOMMENDATION; S: STATUS, PLEASE INDICATE : EXISTING: E, PLANNED: P + DATE

EXAMPLE OF APPENDIX TO "INPUT TO FOLLOW-UP REPORT" Att.# 4

Appendix 11-C

MUPEM's Mandate

MESURE D'URGENCE POUR L'EST DE MONTREAL

CONTINGENCY PLANS FOR MONTREAL EAST

Description	To coordinate municipal and industrial emergency measures plans related to potential chemical accidents which can affect the well being of the public or could cause material damages.
Objectif	.Carry out risk analysis for potential accidents involving dangerous materials. .Identify all responders which could contribute and make sure of their collaboration. .Coordinate a uniform warning system for the responders and the public. .Develop communication procedures to the public in case of an accident. .Coordination of blocking main traffic arteries .Coordination of public evacuation plan .Insure a rapid and efficient response by encouraging better communication between responders. .Promote a better coordination of responders resources.

MUPEM's task is long and difficult due to the large number of agencies involved in this project: risk generating industries, cities, government departments and other.

Note: With the assistance of the APQ, CCPA, the cities of Montreal, Anjou and Montreal East, BPCQ managed to convince his partners (including 27 industries) of the necessity to establish a coordinating committee which will deal with issues related to hazardous materials, in Montreal East. This example of cooperation is known as MUPEM, similar initiatives are being established at Bécancour and Trois Rivièrres.

PORTABLE INSTRUMENTATION FOR ON-SITE ANALYSIS OF TOXIC VAPORS

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ABSTRACT

The Center for Environmental Research at Argonne National Laboratory has developed a versatile toxic vapor analyzer. This instrument, the Chemical Parameter Spectrometer (CPS-100), was designed to detect, identify, and monitor any one of 26-compounds stored in the library, which itself may be updated or expanded (perhaps to >50 compounds). Analysis of the unit performance with a 26 compound library revealed a more fundamental understanding of the analytical performance of the instrument. For example, when identifying unknown vapors, most misidentifications occur between analogous compounds (e.g., benzene for toluene, or trichloroethylene for tetrachloroethylene). This naturally arises from similarities in the physical, chemical and electrochemical properties of such analogues.

While improvements in sensor technology may ultimately alleviate such misidentifications, any selectivity is not necessarily required for emergency or in-the-field applications. Currently under development is a generalized computer algorithm that will classify vapors according to chemical properties based upon the existing sensor array technology. Implementation of such an algorithm would effectively expand the library size and would still provide the user with sufficient data (perhaps class identification of compounds) so as to assess many potential hazards on the spot. The reliability of such a algorithm for "hazard classification" has been evaluated and compared to the present algorithms which selectively identify unknown vapors.

Introduction

Workers involved in the handling, storage, and disposal of hazardous materials are exposed to numerous potential dangerous situations. The personal hazards include exposure to dangerous chemicals (e.g., toxic substances, explosives, corrosives, carcinogens, flammables, or radioactive materials) as well as stresses associated with the physical environment (e.g., noise, heat, cold, etc.) (1). The effect of exposure to any of these potential hazards can be catastrophic and it is essential to assure the safety of all personnel in such environments. To accomplish this objective requires the use of adequate protective measures and adequate instrumentation for the detection, identification and monitoring of all hazards. There are standards set for protective clothing (2) and in the past several years, there have been significant advances in portable instrumentation (3, 4) An ideal instrument for facile chemical analysis for all situations in the field, however, does not yet exist.

Instrumentation and Methods

Instrument Design and Principles

For the past several years, the Center for Environmental Research at Argonne National Laboratory has been developing a versatile portable instrument for the on-site analysis of toxic vapors (4, 5). This instrument, the Chemical Parameter Spectrometer (CPS-100) was designed for use in the field as a means for detection of hazardous compounds. It uses four electrochemical amperometric sensors which respond with different selectivity to various vapors. The choice of sensors is, however, arbitrary, and the CPS-100 has been designed to accommodate the electronic output of almost any sensor system.

In the current prototypes, the analyte is pretreated by four sequential derivation processes (thermal catalyst over a platinum filament heated to 750° C, thermal catalysis over a rhodium filament heated to 700° C, thermal catalysis over a rhodium filament heated to 1000° C, and no pretreatment). The output of the four sensors in response to the pretreatment products produces 16 signals or chemical "parameters". Analysis is based upon comparing response patterns of unknown vapors to the response patterns of previously measured standards.

In its most sophisticated mode of operation, this instrument is capable of identifying and monitoring the level of any one of numerous (> 25) compounds previously measured and installed in the library (in the on-board computer memory). Identification efficiencies of 80-90% have been reported (5) using the instrument. In addition to displaying the identified compound on a LCD panel, a list of possible alternative compounds (based upon the similarities in the library patterns) is also presented to the user. Such a feature is useful in situations in which the operator is confident that certain vapors are not present or when an ambiguity must be resolved. The identification mode of operation is called IDENT. Currently, libraries consist of 26 compounds, but it is possible to update libraries with additional entries, and computer memory for libraries of 50 or more compounds are feasible. There are, in addition, alternative operator controlled modes of operation. In the SELECT mode, the unit is capable of monitoring the concentration of a user-selected compound which is suspected to be present. In addition to providing quantitative information regarding the suspected toxic vapor, an index of reliability is also provided which verifies that the suspected vapor is indeed present. In a third mode of operation (UNIVersal), the instrument will monitor for any vapor which produces a signal over and above the background level. In this third mode, no qualitative information is provide, but the presence of exogenous and potentially dangerous vapors can be determined in a matter of seconds. This mode is used primarily for quick and initial "sniffing" in unknown environments.

Manual operation of the unit is limited to four push button switches which are selected in response to self-explanatory prompts on the LCD display. Subsequent data acquisition, analysis, and display is microprocessor controlled and no further operator skill is required except to insure that the sample is presented to the instrument. Further details on the CPS-100 have been previously presented (4, 6).

Requirements of Portable Instruments for Emergency Applications

While a portable instrument which can accurately identify and quantify a toxic vapor is an essential tool for people working in the field, there are limitations in present technology and currently used designs. As mentioned, there are broad ranges of chemical hazards which need to be monitored and there exists a tremendous variety of different chemicals which can be encountered. The U.S. Coast Guard alone has assembled a list of nearly one thousand compounds which might be encountered in chemical spills (7). Thus the demands on the instrumentation is great, and it is unlikely that a single portable monitor can be developed which can accurately identify all compounds and all types of hazards with 100% confidence in every situation. On the other hand, exact compound identification may not be necessary or even relevant to assure worker safety. What is important, however, is that the workers know what kind of hazard (poisonous, carcinogenic, flammable, explosive, etc.) is present and what the prescribed action should be to minimize risk to personnel, property, and the environment.

Software Expansion of the CPS-100 Capabilities

Chemically Selective Analysis of Compounds

The CPS-100 instrument with its present software package has been proven to be highly accurate in identifying analyte vapors. In a recent study using a 26 compound library, an identification efficiency of 82.6% (8) was obtained. In all cases, misidentification was between analogous compounds, such as benzene for toluene, or trichloroethylene for tetrachloroethylene and the correct compound was always included in the list of possible alternatives. As the library size increases, such misidentifications would become increasingly common. Alternative algorithms can be developed, however, which do not emphasize exact compound identification, but rather categorizes chemicals according to properties or types of hazards (flammable, asphyxiants, caustics, carcinogens, etc.). For the maximum efficiency in grouping compounds by hazard, sensors should be chosen that are selective to the property of interest. While this may not be achievable for all hazardous properties, the presence of many chemical hazards can, in principle, be monitored according to undesirable properties as can be achieved in most combustible gas situations.

The major goals for this study were to: 1.) evaluate and improve the instrument and the array, 2.) develop simple methods to assess the information content of the array, 3) improving our understanding of the theory/principle of operation of the unit, and 4.) find directions to improved device performance in field situations. The specific objective of this report is was to assess the ability of the present system to group compounds by class (i.e. by chemical functionality, by toxicity, by reactivity, or an other chemical parameters) so that one could expand the CPS-100's capabilities.

Analysis by Chemical Grouping

At the present, each library entry consists of a 16 dimensional vector corresponding to the normalized signals from the four electrochemical sensors in the four operating modes. Typically, only a few of the elements in each vector have significant magnitude and the majority of the elements are of a small magnitude. The impressive selectivity of the CPS-100 is achieved by using all 16 channels applying a Euclidean Distance pattern recognition algorithm (9). The analytical significance of a signal, however, generally increases with the signal size since the S/N is better. Therefore, the most reliable (and probably most repeatable) information for each compound is found in the maximum signals. In a simple approach, elimination of all small signals should result in a simplified pattern that can still be generated at low concentrations. The simplified patterns should also retain a significant amount of the chemical selectivity, and should be able to group compounds with similar electrochemical and catalytic properties.

These vectors group the chemicals into 10 separated and distinct classifications as shown in Table 1 with nitrogen dioxide, dichloromethane, and ammonia as separate compounds or groups containing only one compound. Figure 1 illustrates the average 16 dimensional vector for each group of compounds in the library (i.e., after all signals with a relative intensity less than 0.78 are eliminated). The 26 compound library of the unit was modified to eliminate all vector signals that were smaller than 78% of the strongest signal for that specific compound. Thus only major signals for each compound remain in the library.

Considering an assignment into the groups discussed above and using the library as a comparison, 91.3% of the compounds were correctly assigned. This new assignment to the class used the identical data which had previously achieved only 81.6% correct identification efficiency using the Euclidean distance algorithm applied to all 16 (large and small) elements in the patterns for each compound. Using the new library, the only misassignments are in related groups, i.e. between groups 5 and 6. These two groups are, however, similar and could easily merge into a single category. Throughout the testing period, (ca. 6 months), the sensors in the array were very stable and span drift was minimal since constant quantitation of sample vapors was observed. Thus, the stability of the system is apparently adequate for at least six months before recalibration is required.

Table 1*

Group 1
    Carbon Monoxide, Hydrogen Sulfide, Formaldehyde
Group 2
    Acrylonitrile, Nitrous Oxide, Carbon Disulfide
Group 3
    Tetrachloroethylene, Trichloroethylene
Group 4
    Nitric Oxide, Sulfur Dioxide, Acetaldehyde
Group 5
    Acetone, Acetic Acid
Group 6
    Benzene, Naphtha, Propane, Unleaded Gasoline,
    Toluene, Ethyl Acrylate, o-Xylene, Aniline
Group 7
    Ethylene Oxide, Methanol
Group 8
    Nitrogen Dioxide,
Group 9
    Dichloromethane
Group 10
    Ammonia

*The 26 compounds installed into the CPS-100 library and the groups which are formed when only the major sensor signals are used to generate the response pattern.

Conclusions

All tests reported here have been performed under "ideal" situations e.g., constant concentration between 8 - 750 ppm in the laboratory using carefully prepared samples and good laboratory technique. However, this is a first step in assessing the possibilities and the practicality of the technology and these results are extremely encouraging. The sensors, with some engineering and improvement, could easily handle simple field situations. The specific requirements for field use of this instrument is, in fact, being evaluated by the program sponsors (the United States Coast Guard, the Federal Emergency Management Association, the Federal Railroad Administration, and Environment Canada). Intelligent algorithms using classification schemes like the one reported here will speed identification and reduce ambiguity. Class identification and grouping has been demonstrated with software changes and the improvements in sensor technology implemented in this study. This approach can have many applications especially when sensors which respond to different types of stimuli are developed. Toxicity grouping and biological activity groupings could be obtained by designing an array with sensors that parameterize in the dimensions desired (e.g., biosensors which respond selectively to certain classes of toxic substances, asphyxiant sensors, etc. would produce sensors arrays with the kind of selectivity desired by the user).

Support provided by the United States Coast Guard, the Federal Emergency Management Association, the Federal Railroad Administration, and Environment Canada.

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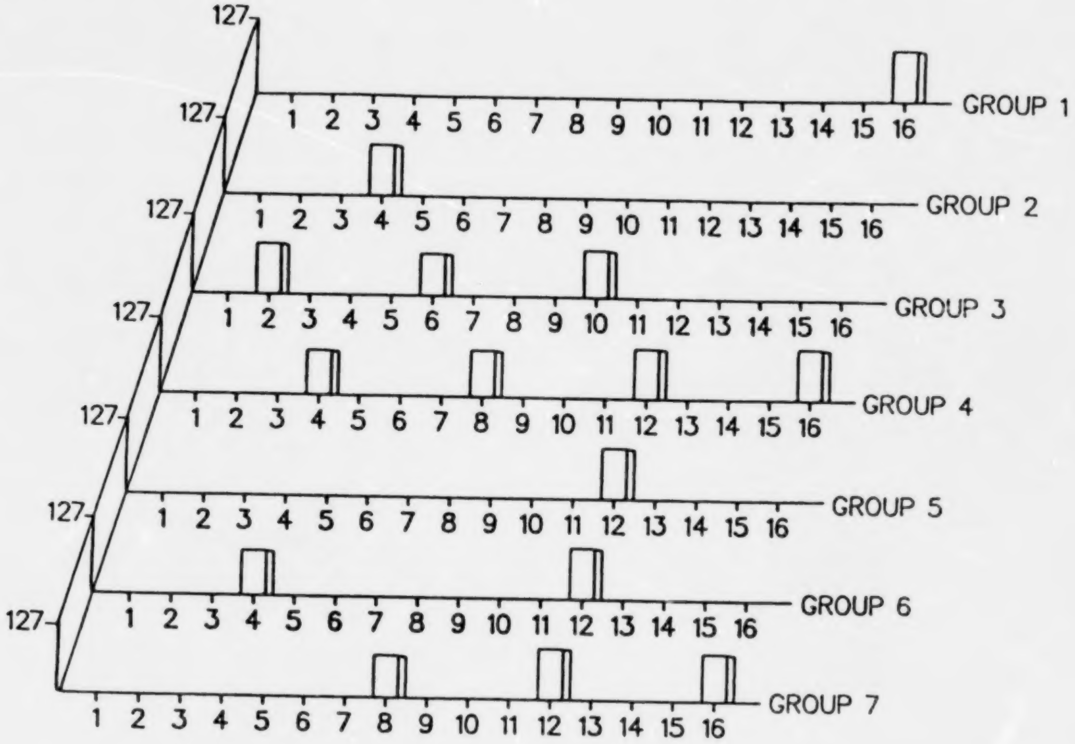

FIGURE 1
Simplified response patterns which resulted from elimination of the low intensity signals as described in the text.

AN UPDATE ON ENVIRONMENT CANADA'S VEHICLE PORTABLE ANALYTICAL SYSTEM

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INTRODUCTION

In the event of a major chemical spill, the quality of the efforts of the spill responders will depend directly on the quality of the analytical systems available to them. Rapid and accurate on-site chemical analysis is necessary to protect the general population, preserve the environment, and minimize property damage. Quantitation as well as identification of the spill materials in various media (air, water, or soil) are necessary in order to determine correct response measures. The Environmental Emergencies Technology Division (EETD) of Environment Canada has had an on-going project to develop analytical systems for spill response. (1) One such system is the Level III or Vehicle Portable Analytical System. The basic concept behind the Level III system is that of a self-contained, mobile unit containing analytical equipment normally found only in a fixed laboratory. Computer data storage and retrieval make possible the rapid and simple identification and quantitation of the spilled chemicals.

THE LEVEL III SYSTEM

The Level III system basically consists of a Perkin-Elmer Sigma 2000 gas chromatograph (GC) mounted in a 1986 Ford cargo van. The modifications made to the van, as well as the system's instrumentation and data systems have been previously described by Mills and Bobra.(2) No major changes to the hardware have been made in the past year. The Level III system provides a mobile, self-contained (power, heat, etc.) laboratory in which an operator can safely obtain fast and reliable answers while remaining close to the spill site. The system has been developed so that a minimum of sample handling is necessary. Accurate results can be obtained by an operator with little formal training in chemical analysis even in an emergency situation. The user-friendly computer software developed for the system both identifies and quantitates an unknown chemical, using its GC trace and a computer library of previously calibrated chemicals.

The Level III system is capable of analysing air, soil, or water samples. Previous work has concentrated on water analyses, primarily by direct injection techniques. For a detailed description of GC conditions for direct injection and the development of the direct injection computer database, see Mills and Bobra.(2) These conditions have remained the same, with the following change to the computer search program. Previously, the operator was prompted for the file of the daily standard (200 ppm toluene) in order to correct for fluctuations in retention time and detector response. The program was altered so that a standard of any concentration may be used, and the operator is prompted for the standard concentration, as well as for the file in which the standard run is stored. Several new chemicals were added to the direct injection library, and spot checks were made on previously calibrated chemicals. See Table I for a list of the chemicals in the direct injection library.

Current work on the Level III system is focusing on the development of a chemical library for headspace analysis. The conditions and methods used in this type of analysis may also be found in Mills and Bobra.(2) There are now over thirty chemicals in the headspace analysis library, listed in Table II. The headspace sampling accessory used in the Level III system is a Perkin-Elmer HS-6 unit. Work on the headspace injection library has not proceeded as rapidly as anticipated due to numerous problems encountered with this unit. In mid-1987 the HS-6 was out of order for a period of months. One of the problems proved to be a capacitor that discharges backwards when the unit is turned on, off, then on again. This discharge blows fuses and eventually causes malfunctions in the control board and the heating unit. The HS-6 circuit board was replaced, however this problem still remains and care must be taken when operating the HS-6 unit.

Problems were also encountered with the power supply to the van. Circuit boards in the air conditioner were affected by voltage fluctuations and had to be replaced. A Sola line conditioner had already been installed in the van to protect the computer, and a second Sola unit was then installed to condition power to all the other outlets in the van.

FUTURE WORK

In the near future, EETD hopes to outfit the GC with a series of high temperature gas switching valves so that the two columns used can remain simultaneously installed. This will eliminate the need to remove one column and install another whenever one wishes to use another injection method. This will render the system much more versatile and easy to use, as well as reducing the amount of time spent configuring the GC.

Plans for the coming year also include continuing development of better methodologies for soil and air testing.

CONCLUSIONS

Work to date has shown that the Level III system is capable of rapid, and accurate results that are simple to obtain. Although chemical analysis is only one facet of spill response and clean-up, it is a rather important one, and we feel that the Level III system would be a valuable addition to any spill response team.

Table I: Chemicals which can be identified and quantitated by direct injection analysis.

- acetic anhydride
- acetone
- adipic acid
- benzene
- benzoic acid
- butanol: 1-butanol
  - isobutanol
  - t-butanol
- butyraldehyde
- caprolactam
- carbofuran pesticide
- chlorobenzene
- chloroform
- cresol: ortho-
  - meta-
  - para-
- cyclohexane
- dicamba pesticide
- dichlorobenzene: ortho-
  - meta-
  - para-
- dimethyl terephthalate
- ethylbenzene
- ethylene dibromide
- ethylene dichloride
- ethylene glycol
- 2-ethyl hexanol
- fenitrothion
- n-hexane
- isopropanol
- isopropylbenzene
- malathion
- maleic anhydride
- methanol
- methyl ethyl ketone
- methyl isobutyl ketone
- methylene chloride
- morpholine
- nonyl phenol
- PCB's: Aroclor 1242
  - Aroclor 1254
  - Aroclor 1260
- pentachlorophenol
- phenol
- phthalic anhydride
- styrene
- terephthalic acid
- terphenyl: ortho-
  - meta_
  - para-
- tetrachloroethylene
- toluene
- 1,1,1-trichloroethane
- trifluralin
- turpentine
- vinyl acetate
- xylene: ortho-
  - meta-
  - para-

Table II: Chemicals which can be identified and quantitated by headspace analysis

- acetic acid
- acetic anhydride
- acetone
- acetonitrile
- benzene
- butanol: 1-butanol
  - isobutanol
- butyraldehyde
- carbon disulphide
- carbon tetrachloride
- chlorobenzene
- chloroform
- cyclohexane
- ethanol
- ethylene dichloride
- 2-ethyl hexanol
- hexane
- isobutyraldehyde
- methanol
- methylene chloride
- methyl ethyl ketone
- methyl isobutyl ketone
- methyl methacrylate
- propanol: 1-propanol
  - isopropanol
- propyl benzene
- propylene oxide
- styrene
- tetrachloroethylene
- toluene
- 1,1,1-trichloroethane
- vinyl acetate
- m-xylene

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ENVIRONMENT CANADA'S PERSON-PORTABLE ANALYTICAL SYSTEM : RECENT FINDINGS

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Introduction

Person-portable systems for on-site quantitative analysis of chemicals following a spill have been designated as Level II systems in Environment Canada's Spill Response program. The Environmental Protection Service selects and modifies equipment suitable for situations in which a single known contaminant is involved. These systems should generate information useable by response teams who do not have extensive chemical training. As well as being simple to use, these person-portable systems must provide results which are accurate and reproducible for analysis in air, water and/or soil media. Chemicals which are of concern are those on the EPS's spill priority list.

Previous work has been published on the testing and modification of the Century Systems Organic Vapor Analyser (OVA), the HNU PI-101 Photoionization Analyser, and the Hach Company Direct Reading Engineer's Laboratory Model DR-EL/4. Recent work has focused on the further expansion and development of the Hach Model DR-EL/4 (Hach kit) as detailed in this paper.

Instrumentation

The Hach kit is designed for the testing of inorganic contaminants and a few organic contaminants in water and soil. It is equipped with a built-in spectrophotometer, a digital titrator, a pH and conductivity meter, glassware and prepackaged reagents. An instruction manual contains procedures for 87 colourimetric and titrimetric tests for which the Hach kit is capable.

Guidelines for the expansion of the capabilities of the Hach kit have been towards increasing the number of test procedures for spill priority chemicals without significantly increasing the number of reagents and pieces of equipment involved. Two examples of modifications to the kit which have involved equipment are: a portable, battery-operated magnetic stirrer which was added to facilitate dissolutions and reactions , and the replacement of the digital titrator in favour of a standard 25 mL buret. The buret is more convenient and reliable and less bulky than it's digital counterpart.

Selection of Additional Tests Considered for the Hach kit

Additional tests considered for inclusion into the Hach kit with expanded capabilities have been subjected to guidelines similar to those involved in the selection of Level II instrumentation. As well as being accurate, sensitive and having a detection range appropriate to the regulations regarding each contaminant, these tests must be straightforward and simple to perform and have a minimum of reagents.

Analytical tests for contaminants found in soil make up a large portion of the recent additions to the Hach kit. Tests accepted for soil analysis must yield results which do not differ significantly for soils with different organic carbon levels since only one calibration curve is used. Extraction of contaminants from soils using water is preferred. Other solvents have been employed where water is not suitable.

More of these additional tests are titrimetric than colourimetric. There was a conscious effort to select a titrimetric test over a colourimetric test. Often wastewater and water from soil extractions are coloured by pigmentation from the soil components such as humic acid. This colouration which is not easily removed by separations (e.g. filtration) can easily interfere with a colourimetric test but does not generally alter a titration endpoint. Also, titrations generally require a minimum of equipment and are quite easy to perform and thus are less susceptible to malfunction and human error.

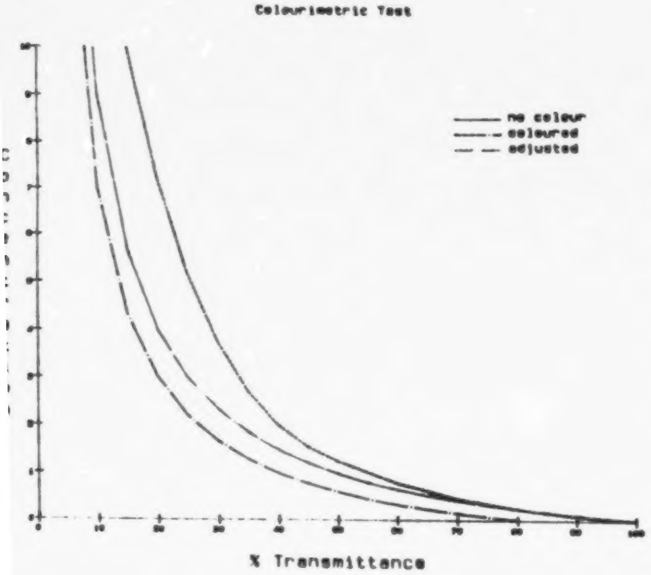

Fig. 1a

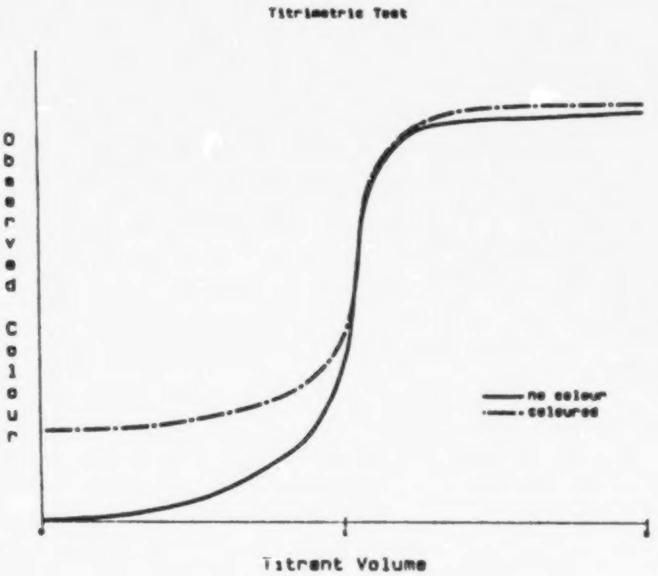

Fig. 1b

The reasons for selecting a titrimetric test are illustrated in the following paragraph. In the colourimetric test (Fig. 1a), at zero concentration the water sample with no visible colour shows 100% Transmittance and as the concentration increases, the %T approaches zero. The sample of coloured water starts at a lower %T but still approaches zero %T in the same way. Adjustment for this curve brings the zero concentration point to 100% T but creates errors for larger concentrations. The colour change in the titrimetric test (Fig. 1b) may be observed differently for coloured water but the change will still occur at the same titrant volume.

New Capability

The expansion of the Hach kit has been concentrated on selecting tests for organic contaminants. The recent work described in this paper and that of Ruttan (1987) previously has added 28 new procedures for quantitative measurement of priority chemicals. These 28 procedures in the expanded kit adds capabilities for analysing for an additional 57 specific contaminants in water and 56 contaminants in soil (Table I). This requires the addition of only 32 reagents to the inventory of the complete kit (Table II). The new capabilities of the Hach kit, with the inclusion of these procedures, are: quantitative tests for 144 contaminants in water and for 56 contaminants in soil.

Two examples of recently added tests are described below.

Titrimetric Test : Morpholine in Soil

This method begins with the extraction of the morpholine from the soil using Methyl Cellosolve. The filtered extraction is reacted with 5 mL of acrylonitrile, 10 mL of methanol and 20 mL of acetic anhydride. Then, after adding the indicator (thymol blue / xylene cyanol FF), the solution is titrated against standardized 0.1N perchloric acid. The total reaction time between collection of sample and titration endpoint is approximately 25 minutes.

Two processes are used to calibrate the results. If a graph is used, the calibration line is valid only for a specific titrant concentration. Alternatively, using an equation for the line, the titrant concentration becomes variable and the test is calibrated for general use. This equation has been set up as follows:

Contaminant Equation-

$$\text{Concentration (mg/kg)} = [\ \#\ \text{mL's of titrant}\ ] \times [\ \text{normality of titrant}\ ] \times [\ \text{Contaminant Factor}\ ]$$

The Contaminant Factor is a numerical multiplier. Each contaminant has it's own unique factor. For the Morpholine in Soil test, the contaminant factor is 11 140.

Table I

Contaminants for which tests have recently been selected for inclusion in th Hach kit:

in soil:
Acetone (C)
Methyl Ethyl Ketone (C)
Methyl Isobutyl Ketone (C)
Formaldehyde (C)
n-Butyraldehyde (C)
iso-Butyraldehyde (C)
Benzene (C)
Toluene (C)
Styrene (C)
Ethylbenzene (C)
Cumene (C)
o-Xylene (C)
m-Xylene (C)
p-Xylene (C)
p-Terphenyl (C)
Phenol (C)
Cresol (C)
Nonylphenol (C)
Hydrogen Peroxide (C)
Urea (C)
Carbon Tetrachloride (C)
Chloroform (C)
Ethylene Dibromide (C)
Malathion (C)
Ethylene Glycol (T)
Propylene Glycol (T)
Ethanolamine (T)
Aluminum Sulphate (T)
Ammonium Sulphate (T)
Copper Sulphate (T)
Potassium Sulphate (T)
Sodium Sulphate (T)
Zinc Sulphate (T)
Aluminum Chloride (T)
Ammonium Chloride (T)
Calcium Chloride (T)
Ferric Chloride (T)
Potassium Chloride (T)
Sodium Chloride (T)
Sodium Chlorate (T)
Zinc Chloride (T)
Polychlorinated Biphenyls (T)
Styrene (T)
Vinyl Acetate (T)
Phthalic Anhydride (T)

in water:
Benzoic Acid (T)
Formic Acid (T)

in water and soil:
Morpholine (T)
Acrylonitrile (T)
Maleic Anhydride (T)
Acetic Anhydride (T)
NTA (T)
Adipic Acid (T)
Boric Acid (T)
1-Butanol (C)
Ethanol (C)
Isopropanol (C)
Methanol (C)

(T)= Titrimetric Test
(C)= Colourimetric Test

Table II

Additional Reagents Required:

Ceric Ammonium Nitrate
Acetic Anhydride
Acrylonitrile
Morpholine
Tetracyanoethylene
o-Tolidine
Sodium Acetate
Ethanol
p-Dimethylaminobenzaldehyde
Sodium Chloride
Barium Chloride
Anhydrous Alcohol
Mercuric Nitrate
Naphthalene
Sodium Metal
Sodium Phosphate
Mercuric Acetate
Sodium Bromide

Solvents:
- Methanol
- Ethyl Cellosolve
- Methyl Cellosolve
- Pyridine
- Methylene Chloride
- Carbon Tetrachloride
- Ether

Standard Solutions:
- 0.100 M Iodine
- 0.100 M Arsenious Acid
- 0.100 M Perchloric Acid

Indicators:
- Thorin
- Thymol Blue/ Xylene Cyanol FF
- S-Diphenyl Carbazone/ Xylene Cyanol FF

Colourimetric Test: 1-Butanol in Water

A colourimetric test has been selected for the analysis of 1-butanol which provides reliable results for a range of 200 to 6000 ppm in water. Development of this test was difficult. A reaction specific to the hydroxide group is insufficient, since the hydroxide group of the alcohols could not be selected from a background of water/hydroxide. This test is exclusive to alcohols and has a short five minutes reaction time. The reaction mechanism involves a substitution with ceric ammonium nitrate. The addition of 3 mL of this reagent in a 25 mL sample is sufficient. This provides a good detection range in water (and also soil).

The optimum wavelength of 450 nm was determined and a linear relationship was established between concentration and absorbance. The information from the calibration curve has been transferred to a meterscale overlay, containing all of the pertinent test information, which can be easily used by the spill responder.

Conclusions

Work on the Hach kit expansion is now reaching completion. The capacity of the kit has been expanded from 87 analytical tests in water to 144 tests in water and an additional 56 soil tests. Promising tests are now being modified for the quantitative testing of several organic halogens in water and soil. The next stage for this project is the packaging development and marketing for the added tests.

Acknowledgements

The author would like to thank Alice Bobra and members of the Environmental Emergencies Technologies Division (Chemistry and Physics) for their help with this project.

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Sniffing Technique to Measure Air Emission Rates from Chemical Spills in Soil

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ABSTRACT

In this paper the theory is presented to establish the benefits of soil-gas measurements in predicting the atmospheric emission rates of volatile organic chemicals from soils. The calculation technique is then demonstrated using data from the literature. During the seminar experimental procedures currently being developed to validate the theory will be discussed.

INTRODUCTION

Atmospheric emission rates for volatile organic chemicals from soil can be important in a number of situations. The chemical may be introduced into the surface soil environment from either a landfill, contaminated groundwater, from intentional application such as pesticides or as a result of a chemical spill. In the case of chemical spills the most likely motive for establishing the air emission rates will be in deciding whether or not cleanup is required. It may also be helpful in establishing the cleanup technique, and in assessing hazard.

Soil-gas measurements can be used to predict atmospheric emissions of volatile organic compounds from soil. Organic contaminants may migrate to the air soil interface and then evaporate through the air boundary layer. In terms of a chemical spill the organic chemical may contaminate the soil to a considerable depth. This chemical may then become a long term atmospheric pollution problem. Direct measurement of atmospheric concentration leads to difficulties due to the spatial and time variations and because concentrations are small large sampling volumes are required to be taken over long periods of time. Measuring the more concentrated and stable soil pore air or soil-gas will lead to greater accuracy, shorter sampling times and increased reproducibility. It may also lead to more consistent application of cleanup criteria.

This paper will focus on the theory and basis for using soil-gas or soil air concentrations as a measure of contaminant emission rates into the atmosphere. The original motivation for the work is to estimate or predict emission rates from landfills; however the work is directly applicable to chemical spill scenarios.

THEORY

The soil compartment of our environment is comprised of three phases. A solid phase, a water phase and an air phase. A contaminant from a chemical spill will distribute itself in all three portions of the total soil environment depending on its physical chemical properties (Mackay 1982; Karickhoff 1981). Obviously a volatile contaminant will partition into the air component of soil to a greater extent than would a water soluble one. The chemical is then capable of migrating through the soil column as a result of bulk motion of the water or diffusion in the water and air phases (Jury 1983). Emission into the atmosphere can only take place from the soil air phase. Thus, any emission must be related to this soil-air concentration and therefore the measurement of this concentration will be useful. The relation between the emission and the concentration involves the transport processes for the compound and for the soil system. This section will develop the relationship.

For simplicity we start with a system in which only diffusional processes are important and the bulk motion of air and water is neglected. The contaminant can flow in either the soil-air or the soil-water to the surface at which point it must flow through the air boundary layer. This configuration is a modification of the classical Whitman Two-Film resistance model (Liss and Slater, 1974). In the classical situation two resistances are in series at an common interface. In the soil air system series parallel resistance exist. The air boundary layer is a series resistance and is typically described by a mass transfer coefficient, K_{AS}, for which a typical value is 0.0028m/s (Mackay, 1982).

$$J_{BL} = K_{AS}\ (C_{ai} - C_{a}) \qquad (1)$$

where J_{BL} is the flux of contaminant through the boundary layer ($g/m^2/s$),
C_{ai} is the concentration in air at the interface (g/m^3),
C_{a} is the concentration in the bulk air (g/m^3).

The two resistances, soil-air and soil-water, are in parallel with each other and are in series with the boundary layer. The diffusion can be described by Fick's Law.

$$J = -D_M\ \delta C / \delta x \qquad (2)$$

where D_M is the component's molecular difffusivity (m^2/s),
$\delta C/\delta x$ is the concentration gradient (g/m^4).

However, the ordinary molecular diffusivity does not apply due to the nature of the soil matrix. To correct for the tortuosity and porosity of the soil a common formulation is that by Millington and Quirk (1959a,b,1961).

$$D_{sA} = D_A \, (\alpha^{10/3} / \phi^{2}) \qquad (3)$$

$$D_{sW} = D_W \, (\Theta^{10/3} / \phi^{2}) \qquad (4)$$

where D_{sA} is the diffusivity in soil air (m^2/s),
D_{sW} is the diffusivity in soil water (m^2/s),
D_A is the molecular diffusivity in pure air (m^2/s),
D_W is the molecular diffusivity in pure water (m^2/s),
α is the air filled porosity (m^3/m^3),
Θ is the water filled porosity ($m^3//m^3$),
ϕ is the soil porosity (m^3/m^3).

To combine the two parallel diffusion paths a weighted average of each must be used. The appropriate weighting requires the use of the partitioning of the compound between air and water phases.

$$D_s = D_{sA} + D_{sW}/H \qquad (5)$$

where D_s is the overall soil diffusivity (m^2/s),
H is the Henry's Law constant for air water.

thus the resulting flux is given by:

$$J_s = D_s \, (C_{sa} - C_{ai})/x \qquad (6)$$

where J_s is the flux of contaminant in the soil layer ($g/m^2/s$),
C_{sa} is the soil-air concentration (g/m_3),
x is depth at which the soil-air concentration is measured (m).

Implicit in equation 6 is the assumption that steady state has been reached allowing for the replacement of the derivatives by the overall differences. By setting the flux through the soil and the boundary layer equal (ie $J_s = J_{BL}$) the flux of contaminant to the atmosphere is:

$$J_T = \{1/[x/D_s + 1/K_{AS}]\} \, C_{sa} \qquad (7)$$

By measuring the concentration of contaminant at a depth x, calculating the "soil diffusivity" and using a typical value of the air-soil mass transfer coefficient it is possible to calculate the emission rate of the contaminant. The concentration will not be measurable at a precise depth and it will be necessary to calculate the concentration at a point x from the measured average concentration over a given depth. One approach will be to base the calculation on the assumption that steady state has been reached at that concentration is linear with depth.

An alternate solution is in the case of the early stages of a chemical spill the concentration will be nearly constant with depth and thus x should be set to zero and the flux reduces to

$$J_T = K_{AS} C_{sa} \qquad (8)$$

It is possible to include bulk motion of the water and air phase. Typically the air phase is limited in the extent of bulk motion that occurs but the water phase is potentially capable of significant bulk motion due to precipitation and the evaporation of water from soil. For simplicity at this stage the bulk motion of air and water will be neglected. The standardized conditions then are represented by a zero net water flux.

APPLICATION

Applying this approach to data produced by Kerfoot (1987) leads to some positive conclusions. Kerfoot used a sniffing technique as a means for identifying the level of contamination of groundwater by chloroform ($CHCl_3$). However as shown in the theory section it is possible to use soil-gas measurements to predict the atmospheric emission rates from soil. In Figure 1 the concentration of chloroform versus depth is shown. It is apparent that the situation that has been set up is approximately steady state. Using equation 5 and appropriate values of diffusivity for chloroform with a soil porosity of 0.6 and a water filled porosity of 0.2 the resultant "soil diffusivity", D_S, is 0.056 m/D. The porosity values used here were not reported by Kerfoot and were selected based on typical and reasonable values. Based on this diffusivity and using equation 7 we get a emission rate of 37 microg/m^2/D. This in itself is not all that significant but what is significant is the accuracy which is likely achieved. Kerfoot reported concentration data of the order of 200 mg/m^3. If you were to take the emission rate and a reasonable wind velocity of 5 m/s an expected atmospheric concentration would be of the order of 1 ng/m^3. The dilution factor is roughly 8 orders of magnitude. It is obvious that the measurement of the soil gas concentration will be significantly more reliable than the atmospheric concentration. The atmospheric concentration is also subjected to numerous fluctuations due to atmospheric stability, wind speed and direction changes. The biggest benefit of a sniffing technique is this increased reliability of the measurement of the soil-gas concentration.

EXPERIMENTAL

The experimental procedures and techniques are currently being developed and as such the description given here is an outline. The objectives of the experiments are two fold. One is to develop and understand a soil-gas sampler. Two, is to measure evaporation rates from a soil system for which the soil-gas concentrations are well known.

Illustrated in Figure 2 is a schematic of the soil-gas sampler. The principal component is a metal tube open at the

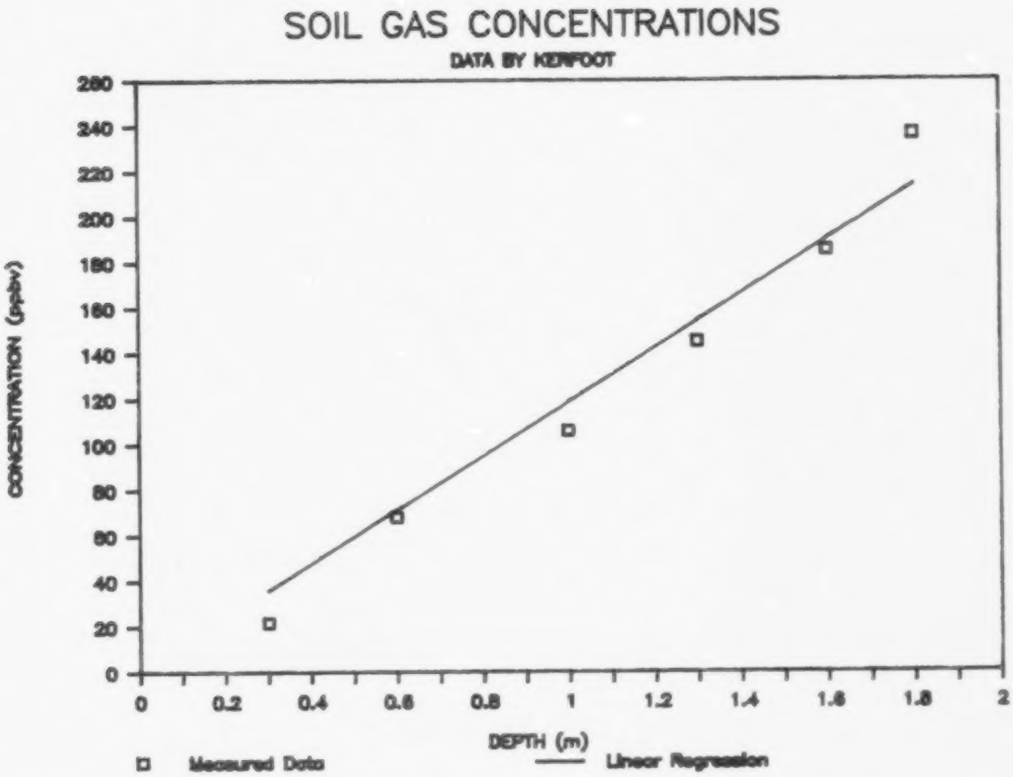

Figure 1. Soil Gas Concentrations as Measured by Kerfoot.

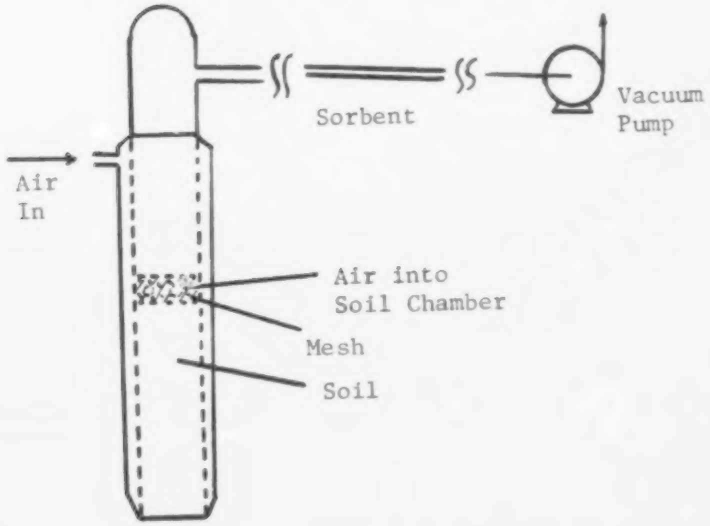
Sorbent
Vacuum
Pump
Air
In
Air into
Soil Chamber
Mesh
Soil

Figure 2. Soil Gas Sampler

bottom to enable it to be driven into the soil. The tube is also fitted with an air inlet system. A small volume of clean air will be used to purge the soil-gas and pass through a sorbent material (tenax, polyurethane foam). The sorbent tube can then be analysed using capillary column gas chromatography. The objectives of this phase is to determine air volumes necessary, effectiveness of the sorbent and the efficiences at various flow rates.

Illustrated in Figure 3 is a schematic of a wind tunnel setup to measure losses from a soil system of known soil-gas concentrations versus depth. The difficult step is the introduction of a soil column of known concentrations into the system. Once this is accomplished the system will be run for a finite period of time and the soil will be analysed for the fraction of the contaminant remaining.

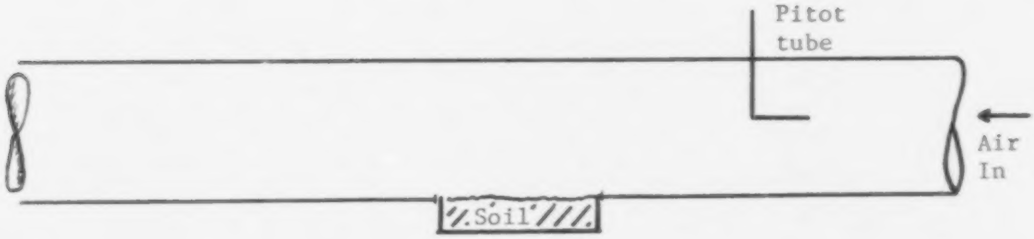

Figure 3. Wind Tunnel for Evaporation

CONCLUSIONS

Theory is presented to illustrate the benefits of soil-gas measurements in the prediction of atmospheric emissions from the soil as a result of chemical spills. The more accurate and reliable measurement of soil-gas concentrations is the prime motivation for using this approach.

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Leak detection system for continuous control of piping in chemical industries

by

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0. SUMMARY

A specially developped temperature and chemical resistant sensor cable permits continuous and low cost control of piping and production facilities in chemical industries, when mounted along the pipes or flanges.
Detecting or transporting medium inside the sensor cable is a neutral gas such as air or nitrogen, therefore the sensing system is intrinsicly safe and applicable even in hazardous atmosphere.
For mounting or exchange of parts of the cable no trained personal is needed.

1. INTRODUCTION

In chemical industries basic chemicals, manufactured chemicals and by-products are transported by means of pipelines over long distances often of several kilometres in length i.e. in discharging a product from a ship into a storage tank placed in asafe area away from the production facility and pumping it later from the storage tank to the production plant.
Other chemicals are directly transported by pipes from one facility to the other.
Therefore the appearance of a typical chemical plant is one of piping-bundles -mostly insulted- totaling several hundreds of kilometres in length (Fig.: 1).

Although the GERMAN chemical industries have already invested billions of Dollars in the prevention of pollution by chemicals, environmental control and the pollution of the NORTH SEA and of the RHINE RIVER have become a political theme over the past few years.

Finally the big fire at the SANDOZ plant in 1986 in Switzerland with an inevitable pollution of the RHINE RIVER has within one year totally changed the public's readiness to accept chemical industries.

RESULT: Accidental leakages are no longer tolerated by the public.

GERMAN authorities have recently (dec. 1987) revised the catalogue of hazardous materials (from 145 up to more than 300) and of hazardous industries (from 800 up to 5000).
In the permits issued by the authorities the permanent control of piping is laid down in a binding manner.

Leaks occur mainly by corrosion, specially after a stand-still or a repair or after cleaning of the production unit, by material defects or by human error.

In general, they are inevitable.

The length, the insulation and the inaccessibility of pipes as demonstrated in FIG.: 1 often prevent the detection of incipient or actual leaks (definition in ‹ 1 › at the right moment, before pollution occurs.
While in some cases a permanent control of flanges and their sealings will be sufficient, in most cases a control system of the whole piping length is desirable.

Such a system has to fulfill the following requirements:

- resistance against the product to protect
- resistance to temperatures up to at least 200 Celsius
  (usual heating medium is 5 bar vapour at 165 Celsius)
- easy mounting and handling
- resistant to mechanical damage
- low cost
- quick and sensitive detection of leaks
- intrinsicly safe

2. LEAK DETECTION METHODS

Several leak detection methods have been reported, such as by YOON et ‹ 1 ›, by GORE ‹ 2 ›, by JOLA ‹ 3 › or by ISSEL ‹ 4 ›.
YOON reports on several methods to detect leaks in pipelines, among these specially pressure loss is used for continuous control of the whole length.
The GORE system is an electric sensor cable system, using the variation of the electric capacity of the cable to detect and / or to locate the leak.
The JOLA system is restricted to conductive liquids, using two electrical cables.
The ISSEL system is based on a tube containing holes, using intermittant air pulses as the transporting and locating medium.

Each of the systems reported on nevertheless has the disadvantage, that either defined lengths cannot be controlled for a reasonable price or that for each repair only specially trained and authorized personnel is allowed (GORE system).
The JOLA system cannot differentiate between acid (product) and vapour or rain at low pH and the ISSEL system cannot -if heat resistant- control each centimetre of a pipe.

3. THE AQUAPHYSIK SENSOR CABLE

Regarding the desired requirements, the AQUAPHYSIK sensor cable is based on a highly flexible hose (FIG.: 2a). Along its axis the hose is sewn with a PTFE thread. This thread, transversing the inner diameter is therefore like the wick of a candle, multiplying the inner surface of the hose.

When a chemical drops from a leaking pipe on the outer side of the hose, it is not only distributed along the hose by capillarity, capillarity also transports the chemical inside the tube. The large surface of the thread permits a quick evaporation, when a neutral gas is forced through the hose. At the end of the sensor cable a detection unit is mounted. This detection unit may be an electric or just a DRAEGER TUBE.

To intensify capillarity of the thread and to diminish the loss of transporting gas by the holes, in the hose finally to protect the sensor cable against mechanical damage, the core hose is surrounded by 2 parallel wires of stainless steel.
These wires may also serve as detection elements in some cases of conductive liquids (FIG.: 2b). Insulated by a special varnish which is either dissolving only in acids or only on in lyes, the wires may be used also as detection medium for the detection of either acid or lyes but not of water.
Moreover the sensor cable is envelopped by a dense glasfiber braiding (FIG.: 3c).
A coloured thread indicates the diameter and the quality of the sensor cable.

Some possibilities for mounting the cable are indicated in FIG.: 3.

4. CHARACTERISTICS OF THE AQUAPHYSIK SENSOR CABLE

Basic testing has been executed with a sensor cable of an inner diameter of di = 5 mm, stich length 6 mm, thread 440 detex, special production.
This cable is heat resistant up to 300 Celsius. Cable length for testing has been choosen to 3 m = 10' resp. 6 m = 20'. FIG.: 4 shows the air consumption and the pressure at the end of a closed sensor cable.
In FIG.: 5 the pressure drop for different airflows is indicated. As the hose transversing threads disturb the laminar flow of the transporting midium, the pressure drop for a 50 m cable of the cited diameter may rise to 70.000 Pa at 800 l/h air flow, because of the REYNOLD'S-number being beyond the value of 2320 (turbulent flow).
FIG.: 6 shows the behavior of the sensor cable at different lengths, when treated with different quantities of 2- PROPANOL.
The results indicate, that the response time is practically independant of the quantity of the product to detect, but depends mainly on the length of the cable.
Caused by the special construction of the cable, the signal output diminishes with the length of the cable, i.g. the longer the distance of the length of the leak from the detection unit, the higher the quantity of the leak product needed.
In practice and specially for the continuous control of piping in chemical industries, this behaviour of the sensor cable is no serious problem, because a pipe, once beginning to leak, fills first the insulation surrounding the pipe before the chemical can affect the environment. And the cable is so sensitive, that 25 meters length need no more than 10-30 ml of product (depending on the vapour pressure of the chemical) to provide an output of a sufficiently high level to produce an alarm.

In FIG.: 7 a similar test with gasoline is shown. In this experiment the sensor had been totally immersed into water for 10 minutes before the gasoline was applied. As the thread, based on PTFE is a very hydrophobic an oleophilic material, this experiment indicates clearly that the sensor cable attracts the gasoline and displaces the water in the thread.

Therefore this sensor cable system can also be operated in water, where it is able to detect organic solvents i.g. in waste water, for controlling effluents of heat exchangers etc.

5. SUMMARY

The AQUAPHYSIK sensor cable specially designed for the detection of leaks in chemical industries as described by the example of a cable with an inner di = 5 mm can easily be adapted to other diameters, other lengths and other applications. It is heat resistant up to 300 Celsius and can be mounted or exchanged by untrained and unauthorized personel.
Each suitable detection unit can be run with this cable. A connection to process control systems is possible. Its sensitivity of some millilitres per metre is so fine that already the beginning of a leak will be detected before pollution of the environment really occurs.
For this system patents have been applied for.

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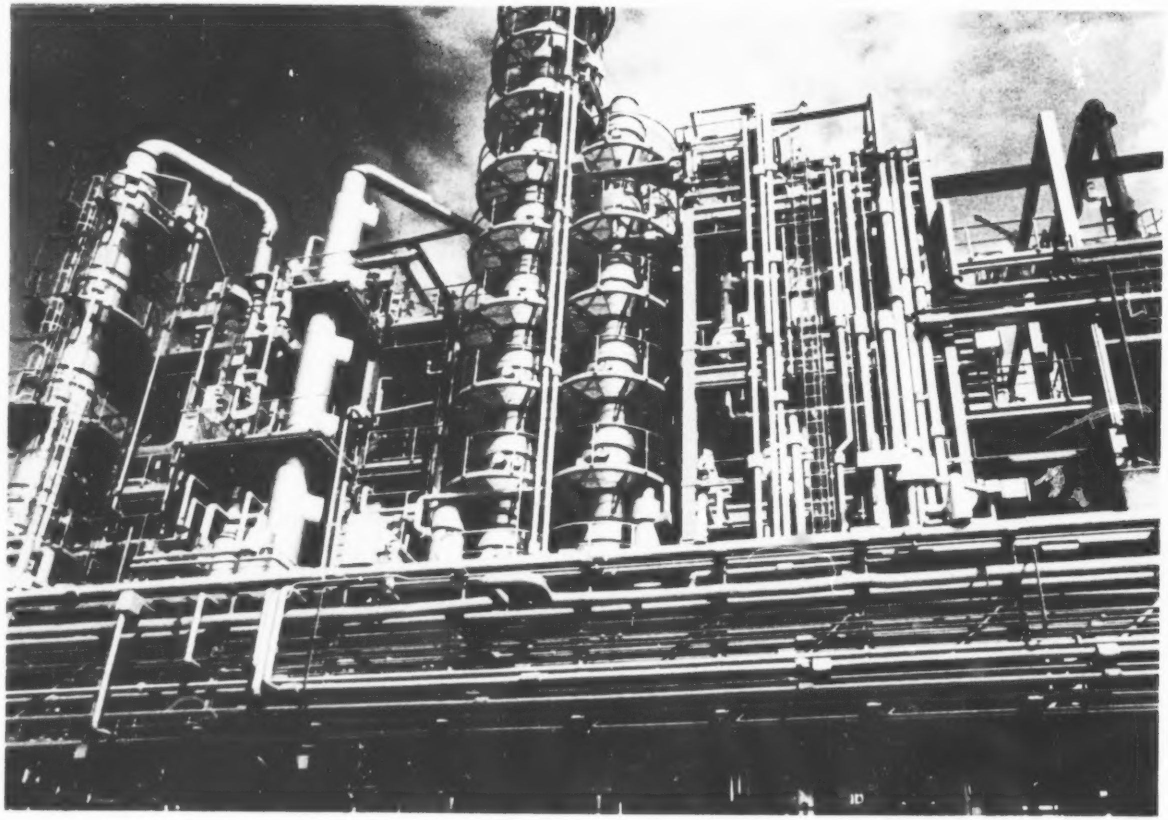
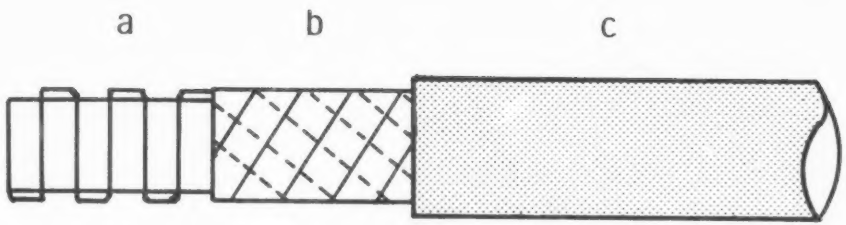
FIG.: 1



PIPING IN
CHEMICAL INDUSTRY

FIG.: 2

SENSOR CABLE



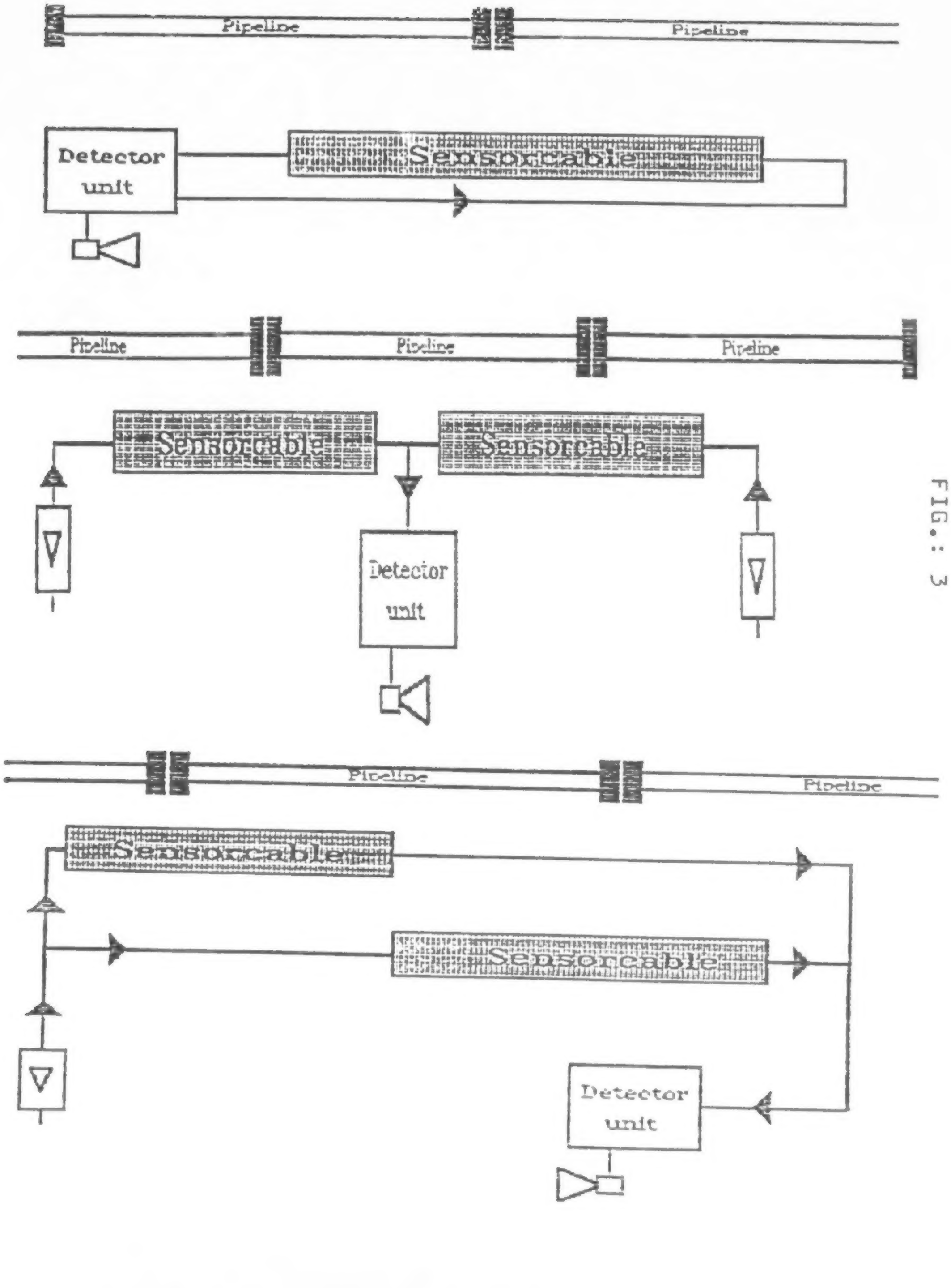

Pipeline
Pipeline
Detector unit
Sensorcable
Pipeline
Pipeline
Pipeline
Sensorcable
Sensorcable
Detector unit
Pipeline
Pipeline
Sensorcable
Sensorcable
Detector unit

FIG.: 3

FIG.: 4

SENSOR CABLE

AIR CONSUMPTION VS PRESSURE

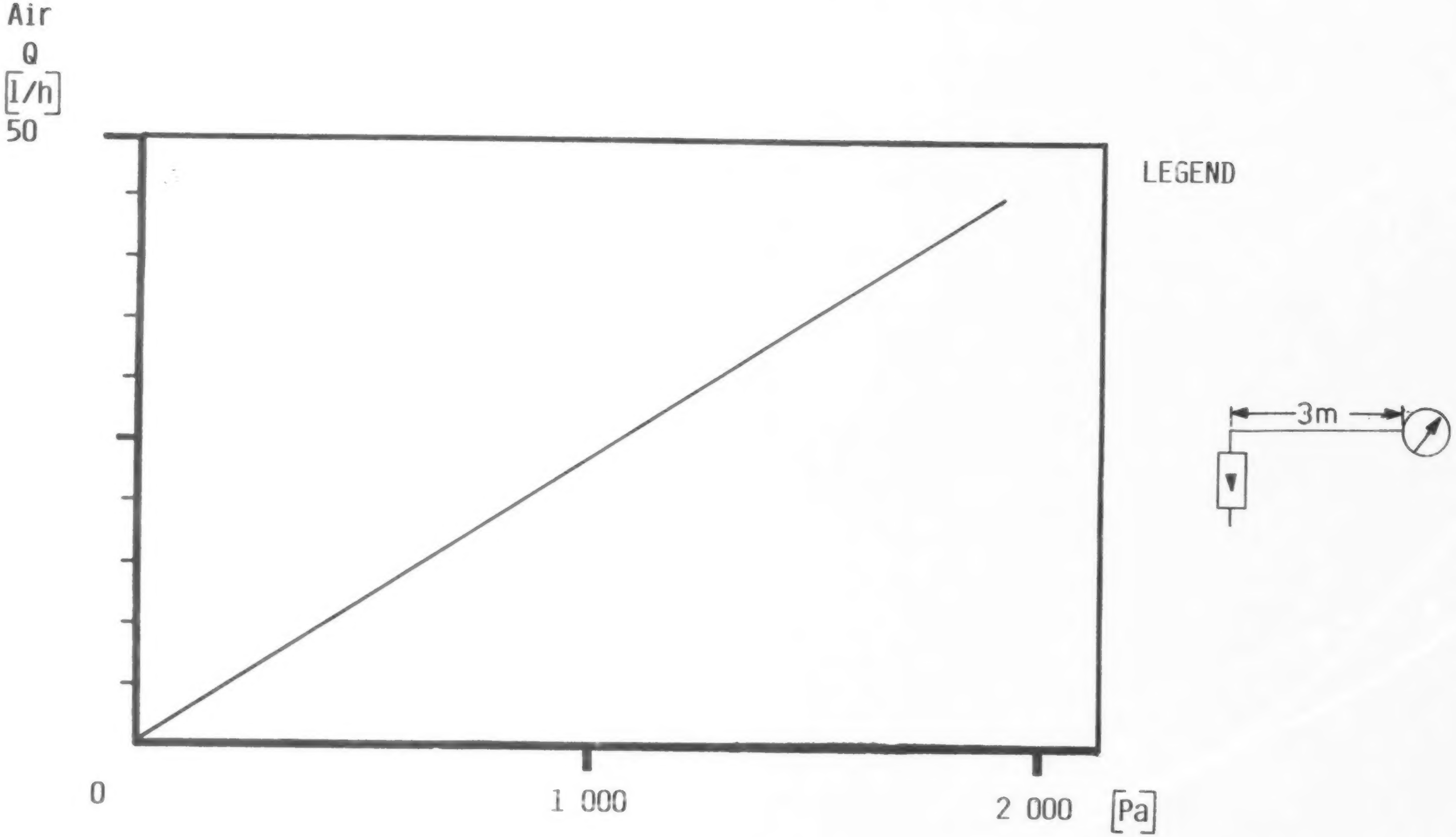


FIG.: 5

SENSOR CABLE

PRESSURE DROP WITH OPEN CABLE ENDING
for different air flow

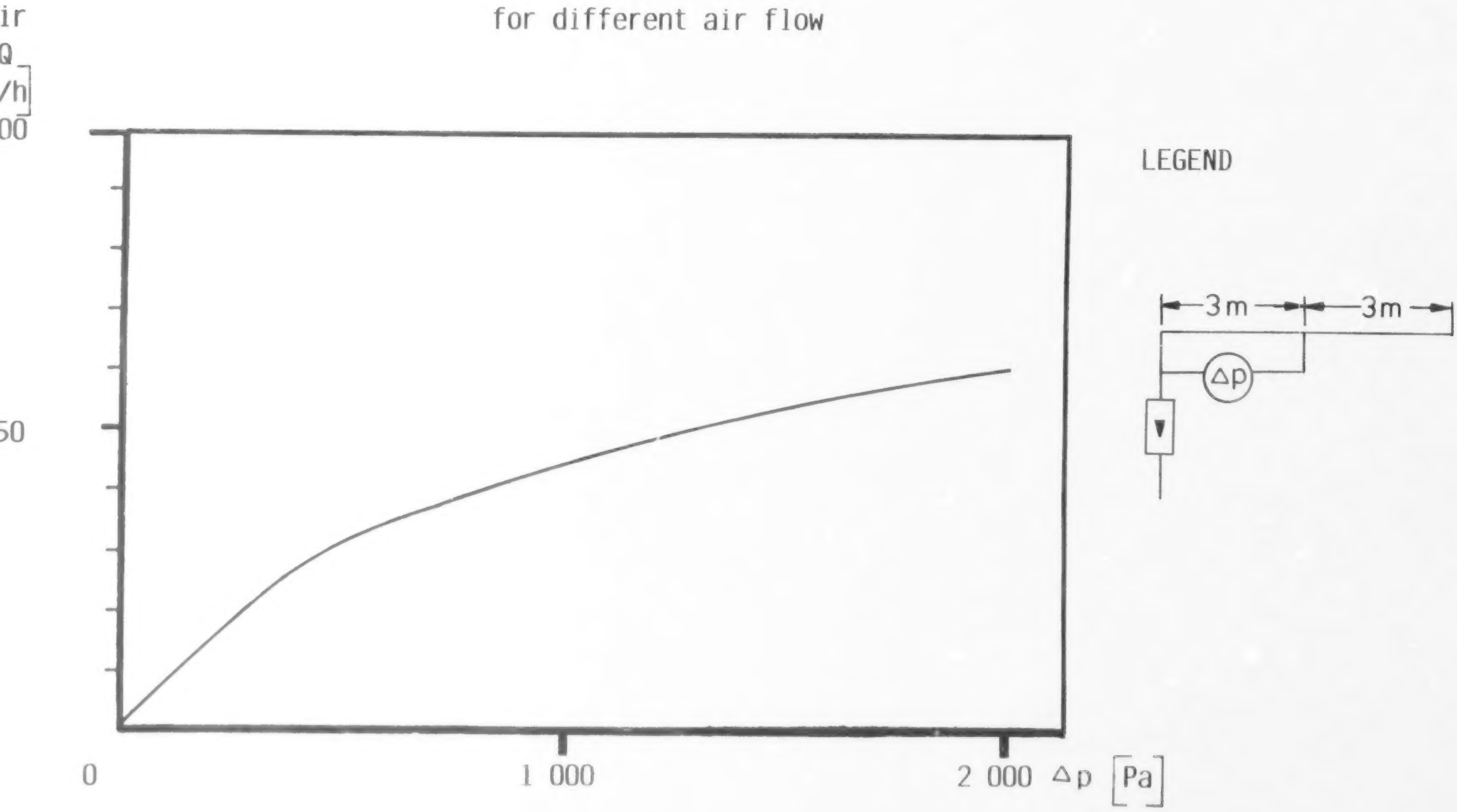


FIG.: 6

SENSOR CABLE

TEST WITH 2-PROPANOL

at different lengths
Qair = 60 [l/h]

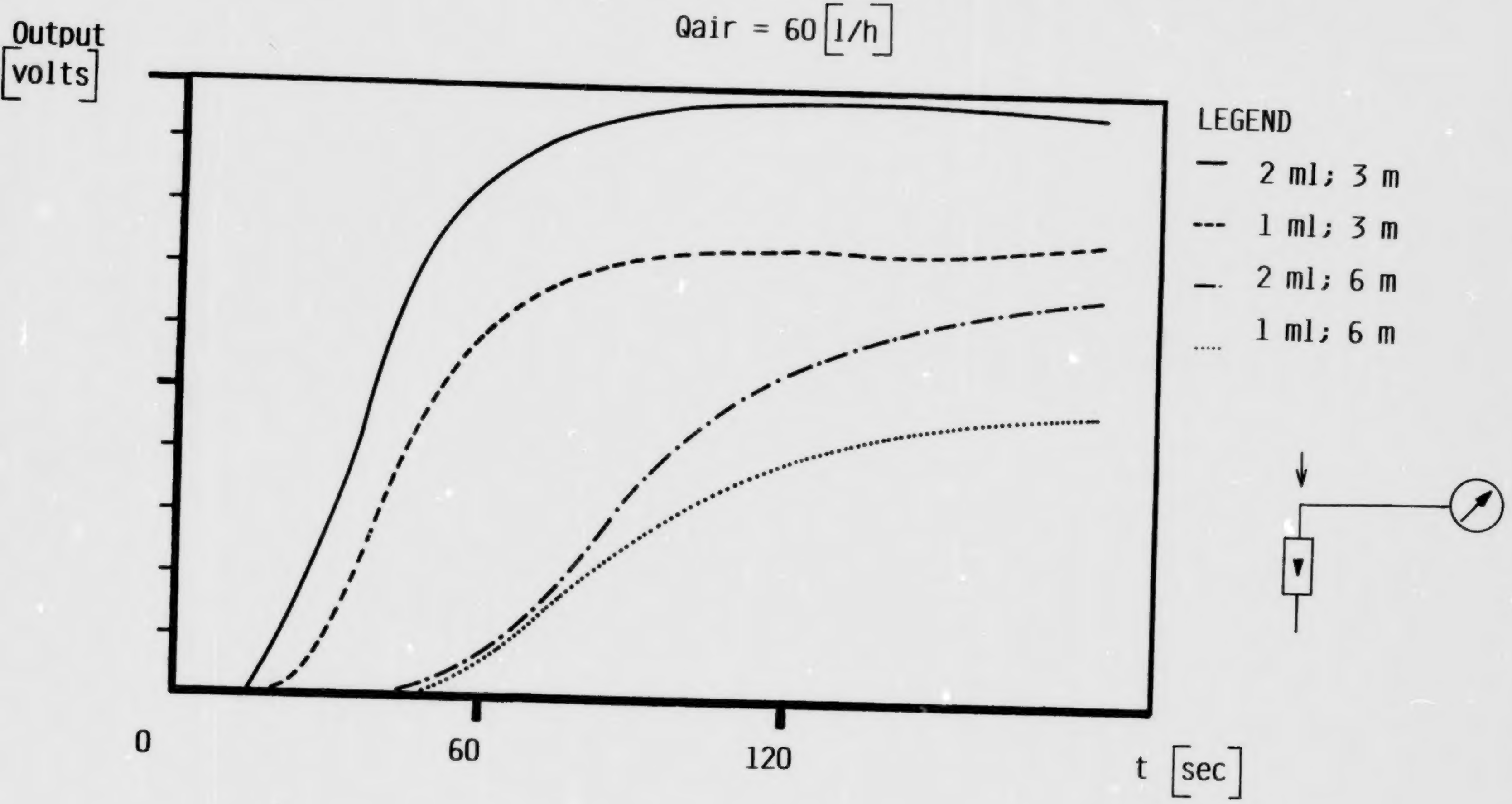
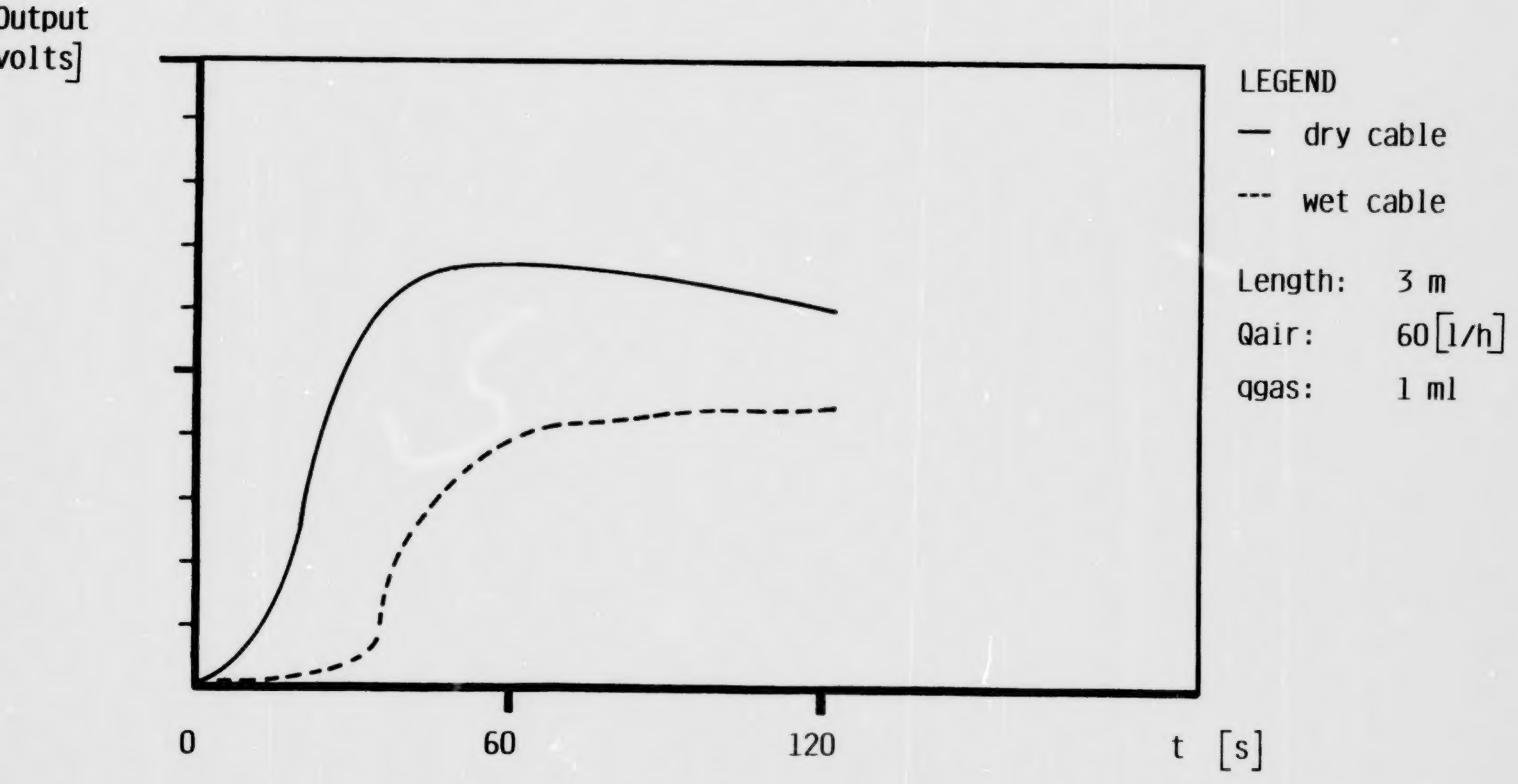


FIG.: 7

SENSOR CABLE

GASOLINE SUPER

dry cable vs. wet cable



REMOTE CONTROL EXTREME EMERGENCY ANALYTICAL SYSTEM

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The development of the remote analytical and sampling system discussed in this paper was initiated and funded by the Environmental Emergencies Technology Division (EETD) of Environment Canada. This system was developed to complement the vehicle–portable analytical program also developed by EETD. The primary function of the system is to assist in the response to spills of highly toxic and volatile chemicals without endangering the lives of response personnel. The system has been designed to retrieve air samples above the discharge location, and transmit a video record of the accident site and real–time pollutant concentration measurements to a location remote from the spill site. The collected air sample will be analysed using the capabilities of the vehicle–portable analytical system. The real–time pollutant concentration and video record of the over–flown area will be used to identify the extent of the toxic plume.

GENERAL SYSTEM DESCRIPTION

The remote sampling system consists of the following major components:

1) Radio controlled model helicopter (equipment platform);
2) Photoionization Detector (for real–time pollutant detection);
3) Air sampling pump and collection tube (for gas sample collection);
4) Video camera and transmitter (for site inspection, platform positioning); and
5) A receiving ground station (T.V. and video recorder to view real–time and record events/PID output.

The helicopter platform enables the user to transport the photoionization detector (PID) and gas sampling equipment to and from a hazardous location without threat to the health of the spill responder. The video camera and transmitter installed on the helicopter relays the location of the monitoring equipment back to the operator's location. It also transmits the real–time PID output (via the audio portion of the video signal) back to the ground station. The gas sampling pump is turned on and off by channel 5 on the helicopter's control transmitter thus giving the operator the ability to vary the volume of gas sampled. The video signal can also be recorded at the ground station for review after the flight.

These major components are discussed more fully in the following paragraphs.

Model Helicopter

The helicopter used in this system has been custom built to provide a payload capacity of approximately 7 kilograms. The rotor mechanics were taken from a commercially available kit (manufactured by Heim) and strengthened by replacing all connecting rods and swivels with heavier components. An 18 cubic centimetre displacement model glow engine is used to power the aircraft. The complete air–frame and cowlings had to be custom designed and constructed to accommodate this engine. The helicopter is controlled by a Futaba digital proportional radio control system model #FP–7FGH.

Photoionization Detector

The photoionization detector (PID) installed on the helicopter is Photovac Incorporated's TIP II air analyzer. We have removed the TIP's battery pack and power it from a central power supply. The output from the TIP is transmitted to the ground station via the audio signal of the video transmission. This is accomplished by first converting the TIP's output voltage level to a frequency on the helicopter, sending this audio signal to the ground station and finally converting this frequency back to an output voltage for display.

Air Sampling

A Gillian air sampler (model HFS IIB) has been modified to perform the air sampling duties on the remote system. The Gillian pump, flow metering components and control electronics have been stripped from their original plastic housing to reduce the size and weight of this assembly. The pump is powered by the central battery supply and is turned on and off by an electronic switch controlled by channel 5 of the helicopter radio control system. This allows the user to vary the quantity of air pumped for each sample.

Video Camera, Transmitter and Ground Station

A Panasonic model WV–D5000 colour video camera is mounted on the front of the helicopter to provide a view directly under the helicopter. A 50 mm fixed focal length, auto–aperature lens has been selected for this application based on approximate operating altitudes and a reasonable field–of–view. The video signal is sent to the ground crew via a commercially available transmitter that transmits on channel 14. To achieve a reasonable range of operation (approximately 1.5 km) an amplifier has been added to this transmitter. The signal is picked up by a standard TV set and recorded on a VHS format video recorder for future reference. The PID output is abstracted from the audio portion of this signal (via the TV's ear phone jack) and the pollutant concentration is shown on a separate digital display.

The complete system has yet to be fully tested at this time. The helicopter has seen several hours of service and many successful flights. Several minor helicopter design weaknesses have been identified and corrected as a result of this testing. We are now quite confident of the performance of this helicopter platform in the hands of an experienced operator. The video camera, PID and gas sampling systems are all in place and ready for use but have not been tested fully in field situations. Delays in receiving the video transmitter amplifier has prevented this final testing of the system.

MONTANA MINING TOWN -
RESIDENTIAL MERCURY VAPOR MONITORING

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INTRODUCTION:

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to Federal On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters, and Regional Offices, as well as other United States and Foreign Governmental Agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

Although this paper briefly describes the past gold and silver mining techniques used in this Montana area and EPA Region VIII's site assessment efforts, the main theme is a summary of ERT's residual mercury vapor monitoring protocols. The paper describes the residual mercury vapor monitoring plan using both real-time hand held instruments and laboratory analytical methods. In addition, it will present the data received during Phase 1 (winter conditions) and Phase 2 (summer conditions) sampling.

BACKGROUND:

The site is located within a historical mining district in Southwest Montana. From the early 1880's until 1910 three mills operated at the site, processing ores from several mines in the vicinity, silver was the primary mineral removed. In the process mercury and water were mixed with the pulverized ore to form an amalgam; the wastes were decanted and the liquid metals were drawn off the bottom in settling pans. Waste rock, overburden and tailings material from the mining and milling operations were discarded in huge piles adjacent to the old mill sites. The waste piles are estimated to contain over 5,500,000 cubic yards of material. Analytical results from samples taken of the waste piles and surrounding soils indicated elevated levels of arsenic and heavy metals, including cadmium, lead and mercury.

Since the initiation of mining in the area, the community has been established and grown around the waste piles. Approximately 70 to 100 homes are directly affected by surface run off and erosion of the waste piles, as well as wind blown contaminates. Additionally, one mill was demolished by fire in 1906 and an unknown volume of mercury was released. In the late 1930's a baseball field was constructed on the site of the fire by leveling off a waste pile and installing a backstop. Soil samples taken at the site contained visual evidence of elemental mercury. The extent of mercury contamination is further supported by reports from long time residents of mercury being recovered from drainages by children in quantities large enough to sell to local assay offices.

REGIONAL SITE ASSESSMENT:

SITE BOUNDARIES: From soil samples of the baseball field taken by the Montana Bureau of Mines and Geology, elevated levels of heavy metals in a public area were identified. The EPA's Region VIII Emergency Response Branch was requested to conduct site assessment and implement measures to mitigate the threat to public health. The project area was determined by the location of the mill dumps historically documented to have utilized mercury as an amalgam in silver and gold ore processing. After identifying the waste dumps, the surface drainages from the dumps were followed and included in the project area.

CORE SAMPLES: To further delineate the extent of contamination six hundred and eleven (611) core samples were collected by EPA, using a truck mounted auger drill rig and split spoon sampler, from sixty-three (63) sample locations. The core samples identified eight areas of concern where contaminants were concentrated in the waste dumps and drainages down gradient from the dumps. Hand slotted PVC pipe was placed in the majority of the sampling holes to allow personnel from the ERT to collect mercury vapor samples from the core samples locations. These real-time sample results taken during drilling were used both to determine the level of personal protection for sampling personnel due to potential exposure, and the extent of mercury contamination in the soil. Due to the proximity of the mineralized vein to the surface, elevated levels of metals naturally occurring that are not impacted by past mining and milling activities were identified by the presence of mercury, which is not naturally found in the area. The presence of mercury was an indication of wastes associated with the milling of the ores.

COMMUNITY INTERVIEWS: A total of 125 homes was potentially impacted by migration of the waste piles, and were within the project area. Interviews with the residents were conducted in order to determine the impact of the heavy metal contamination, gather further background information, answer questions or concerns regarding EPA's action, and obtain access for sampling on residential property. All interviews were arranged at convenient times for the residents.

SURFACE YARD SAMPLES: A total of 133 soil samples were collected from the residential yards located within the site boundaries. The samples were collected at the surface or immediately below the root zone, where appropriate. A uniform two foot by five foot grid was laid out along or within a pathway near an entrance to the home, and a composite sample was collected from each corner and center of the grid. In addition to the composite sample, a bias sample was collected in yards where mine wastes were suspected. An action level of 2000 mg/kg was established for yards over that level to be addressed in the removal action, 20 yards were identified exceeding this level.

ANION SAMPLES: Twelve surface soil samples were collected from drainages within the area and analyzed for chloride, carbonate, sulfide, sulfate, nitrate and nitrite as nitrogen. The samples assisted in determining the ability of the metals to migrate within the soils.

ENVIRONMENTAL RESPONSE TEAM'S INVOLVEMENT:

RESPONSE ACTIVITY: U.S. EPA Region VIII requested technical assistants from the ERT in the area of developing and implementing a residential mercury (Hg) vapor surveillance plan. This task was complicated by the fact that the only recognized indoor sampling technique was designed for workplace monitoring, and analytical techniques were not available commercially. Therefore, a decision was made to combine various NIOSH procedures to accomplish the goal. In addition to the laboratory results, it was decided to utilize real-time field instruments to spot check the residential areas as well as locate the potentially highest concentrated areas for sampling.

MERCURY VAPOR SURVEY: For this investigation a real-time gold film Mercury Vapor Analyzer was utilized as a Hg surveillance device. The instrument operates on the principle of selective absorption of Hg onto the surface of a thin gold film. This results in an increase in resistance across the gold film. The change in resistance is linear in nanogram concentrations of mercury. This is compared internally to reference gold film through a microprocessor.

The residential survey with the real-time analyzer involved a minimum of two survey locations: 1. Basement/crawl spaces; 2. Living spaces. Each of these survey points were subdivided into an area less than 1 ft. off the floor and the breathing zone (4 ft. to 6 ft. above the floor). At each survey point and its respective subdivision a minimum of four instruments readings were taken. The average reading obtained was later reviewed in the decision making phase.

Since winter and summer ambient temperatures are so extreme in Montana, the residential sampling was conducted in two phases. Phase 1 was during the winter when houses were sealed up and the sampling crew experienced extremely cold weathe (-35 Degrees F). Phase 2 was during the summer when ambient temperatures were milder and houses were opened.

SCRAPE/VACUUM SAMPLING: The procedure for taking scrape samples in basement/crawl spaces with earth floors was as follows: an appropriate area was scraped with a plastic scraper until at least a four gram sample was collected and the dimensions of the sampling area recorded. Scrape samples were collected and stored in sealed 40 ml glass vials.

When solid or carpeted floors were encountered, the sampling technique involved the use of a specially modified vacuum device. The vacuum was modified in such a manner as to prevent cross contamination between samples. This was accomplished by only allowing the samples to contact clean filters. Analytical constraints required a minimum sample of 4 grams. Due to the fact that dust conditions varied significantly from house to house it was necessary to vacuum an appropriately sized area in order to collect a sufficient sample. Since this type of Phase 1 data was not useful to the decision making process, it was not repeated in Phase 2.

SAMPLING DECISION LOGIC: The sampling decision logic determined whether or not a house required additional investigation. Although the Threshold Limit Value for mercury and the practical detection limit of the survey instrument were considered while establishing the selection criteria, field use and bench tests indicated that readings below 0.002 mg/m3 may represent false positive results while readings above this level were generally yielded true positive results. Therefore, additional sampling was mandated when an average reading in excess of 0.002 mg/m3 occurred. This additional sampling included air sampling and scrape/vacuum sampling during Phase 1 efforts. However, only air samples were collected during Phase 2 activities.

ANALYTICAL PROCEDURES:

PHASE 1 mercury air samples/collection system consisted of a two part filter system. The initial segment consisted of a 13mm Glass Fiber Type A/E prefilter. This in turn was attached to a NIOSH Chromosorb B Mercury Collection Tube. The filters and the tubes were treated as individual samples.

The method of analysis was a modified version of NIOSH Method, P & CAM 165. Sample analysis was modified as follows:

1. Place tubes or filters into individual 50 ml volumentric flasks.
2. Add 5 ml Aqua Regia and digest 30 minutes swirling occasionally.
3. Dilute to volume using D.I. water.
4. Pipet 25 ml of digested sample into the BOD bottle.
5. Dilute to 100 ml with 10% Nitric Acid.
6. Add 5 ml stannous chloride solution immediately prior to bubbling for analysis.

The results were calculated based on the following equation:

$$\frac{\text{ug Hg per sample}}{\text{12L}} = \frac{\text{ug}}{\text{L}} \times \frac{\text{1mg}}{\text{1000 ug}} \times \frac{\text{1000L}}{\text{cubic M}} = \frac{\text{mg}}{\text{cubic M}}$$

PHASE 2 mercury air samples/collection system consisted of two air sampling methods for mercury: NIOSH Method 6000 and NIOSH Hopcalite Tube method (proposed).

NIOSH METHOD 6000: Method 6000 uses a two part filter system consisting of a 13 mm Glass Fiber Type A/E prefilter and a NIOSH Chromosorb B Mercury Collection Tube. The filter and tube could not be analyzed by Method 6000 because the equipment is not available outside of the NIOSH laboratory. Therefore, the method of analysis was a modified version of the NIOSH Method, P & CAM 165 mentioned above.

NIOSH PROPOSED HOPCALITE TUBE METHOD: This method used a glass tube containing Hopcalite coated with silver. The analysis of the absorbent is accomplished by using the modified P & CAM 165 method.

MONTANA MINING TOWN RESULTS AND DISCUSSION:

The indoor residential air sampling strategy developed for determination of mercury contamination in Montana Mining Town has been based upon real-time monitoring and laboratory analytical techniques.

The real-time monitor was used for health and safety monitoring and as a means of screening potential sampling locations. Air samples were collected in areas where real-time reading indicated elevated mercury concentrations.

Two air sampling and analytical techniques were employed for the residential mercury study. The air samples were collected according to their respective methodologies.

Table No. 1 presents the data for the samples that contained mercury at levels greater than the detection limit. Table No. 2 provides information regarding the total number of samples analyzed.

The author's original intentions were to evaluate the real-time mercury monitoring device as a screening tool for low concentrations of mercury in air by comparing the real-time readings with accepted analytical methods. Regarding this evaluation, the results obtained are inconclusive. Since the number of sampling points with significant Hg concentration is limited, it is difficult to determine even general tendencies.

CONCLUSION:

The analytical results indicate that the observed real-time mercury measurements frequently indicate low level false positives. At this point the authors propose no explanation for the false positives.

One area which warrants mention is the correlation between the modified NIOSH Method 6000 method and the proposed NIOSH Hopcalite Tube method. Once again, the number of samples with reportable concentrations of mercury is limited. This hampers the determination of a definitive correlation between two sampling methods. However, the two methods appear to provide similar results.

A review of the air sampling results indicates a seasonal variation in the indoor residential mercury concentrations in the air. The air sampling conducted in January (Phase 1) indicates 10 samples with reportable concentrations of Hg; while the July (Phase 2) survey provides only two positive results. There are numerous factors that may contribute to this variation. To be sure, temperature, pressure and humidity effect the mercury concentrations. The amount of ventalation a confined area receives also affects the mercury concentrations. There are too many variables to determine which factor(s) are responsible for the seasonal variation.

The authors hope other field response individuals find this summary of the "Montana Mining Town - Residential Mercury Vapor Monitoring" techniques useful. The procedures mentioned are currently being used by ERT and are continuously being updated and modified for each specific response.

ACKNOWLEDGMENT:

The authors express their appreciation to all members of the US EPA's Environmental Response Team and US EPA ERT-TAT Technical Assistance Team and Environmental Emergency Response Unit Contractor for their many contributions and constant updating of our monitoring program. TABLE I.

SAMPLES WITH DETECTED MERCURY CONRTENTR IN AIR

(Concentrations reported as mg/m^3)

Sample No.	Hopcalite Method	Method 6000	Average Real-time Reading mg/m^3
Detection Limit	0.001	0.002	.005
PHASE 1 SAMPLE #		CONC. Hg mg/m^3	
111-L1-T		.00333	*
067-B-4TA		.0242	*
067-B-5TA		.00167	*
067-L-4TA		.00750	*
067-L-5TA		.0142	*
063-B-4TA		.00167	.001
063-L-5TA		.00667	.009
FB3		.00167	-
FB5		.00333	-
BG17-L-5TA		.00333	*
HASE 2 SAMPLE #			
070-B1		0.003	0.01
068-B1		0.002	0.004

* Below My Detection Level

- No monitoring conducted

TABLE NO. 2 - TOTAL NUMBER OF SAMPLES ANALYZED

	# of Samples Analyzed NIOSH Method 6000	# of Samples w/Hg conc. above detection limit method 6000	# of Samples Analyzed NIOSA Hopcalite	# of Samples w/Hg conc. above detection limit Hopcalite Method
Phase 1	120	10	-	-
Phase 2	22	2	67	2

CHEMICAL EXPOSURE INDEX

John Easterbrook
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INTRODUCTION

The Chemical Exposure Index (CEI) provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents. This index is intended to be a simple, empirical rating of the acute toxic hazards from chemicals in a comparable and quantitative manner. It can be used as the basis for establishing both the frequency and depth of review needed to properly evaluate the particular toxic release hazards, prevention and mitigation in any individual "fixed" or stationary unit.

The CEI formula takes into account five factors which influence the magnitude of exposure from any potential release:

1. Toxicity (Acute Health Hazard Rating)
2. Quantity (Volatilized Portion)
3. Distance (to each area of concern)
4. Molecular Weight (relates to Vapor Density and Vapor Dispersion)
5. Process Variables (Temperature, Pressure, Reactivity)

Each of these factors have been categorized into directly proportional scale numbers to maintain quick and simple calculations by eliminating any nonlinear or logarithmic effects. Absolute measures of risk are very difficult to determine, but this system will provide a method of ranking one risk relative to another. It is not intended to define a particular containment as safe or unsafe or acceptable or unacceptable. This procedure will focus attention on the necessary degree of concern and will provide the opportunity for recommendations, improvements, and concurrences from appropriate knowledgeable people. Note that flammability and explosion hazards are not included in this index.

CHEMICAL EXPOSURE INDEX

List of Contents

Chemical Exposure Index

Chemical Exposure Index Summary

Definitions of Scale Numbers

- Acute Health Hazard
- Vapor Quantity
- Distance
- Molecular Weight
- Process Penalties

Review Procedure and Checklist

Containment and Compliance Checklist

Figure 1 - Acute Health Hazard Scale Number Graph

Table I - Table of EEPG's and Acute Health Hazard Numbers

Appendix I - List of Some EEPG's used by Dow

Appendix II - Scenarios for Estimation of Release Rates for Calculating CEI

CHEMICAL EXPOSURE INDEX

PLANT ______________________________ LOCATION ______________________________

CHEMICAL (One per Index) ________________ TOTAL QUANTITY IN PLANT ________

LARGEST SINGLE CONTAINMENT ________________ TEMP. OF CONTAINMENT ________

PRESSURE OF CONTAINMENT ________________ BOILING POINT ________________

FLASH POINT, °C ________________________ MOLECULAR WEIGHT ________________

EMERGENCY EXPOSURE PLANNING GUIDELINE (EEPG),
SEE TABLE I & APPENDIX I. ______________________________________

I. Complete the Chemical Exposure Index Summary and show highest CEI to the Public ----------------- ☐

This CEI number determines the level of review needed as follows:

0 to 100	Internal review - Superintendent and Major Manager review and sign every two years.
100 to 300	Site Review Committee, Superintendent and Major Manager review every two years.
300 to 400	Area Representative and the preceding group review every two years.
Above 400	Corporate representative and the preceding group review every two years.

II. Complete Chemical Exposure Review Checklist, prepare Review package, and indicate date ready for further reviews. (Will be scheduled with Loss Prevention Contact) ____________

III. List any Sights, Odors, or Sounds which might come from your facility and cause public concern or inquiries (e.g., smoke, large relief valves, odors below hazardous levels such as mercaptans or amines, etc.)

____

____

Reviewed by:		Date
Plant Supt. or Manager:	____________________	____________
Major or Gen. Manager:	____________________	____________
Site Review Representative: (If Public CEI is above 100)	____________________	____________
Area Review Representative: (If Public CEI is above 300)	____________________	____________
Corporate Review Representative: (If Public CEI is above 400)	____________________	____________

CHEMICAL EXPOSURE INDEX SUMMARY

Complete the following Table (See Note 1) by filling in and multiplying the appropriate Risk Factor Scale numbers for each of the major Risk areas as identified in the following formula (See Definition of Scale Numbers on next page):

I.	X	II.	X	III.	X	IV.	X	V.	=	VI.
ACUTE HEALTH HAZARD SCALE NO.		VAPOR QUANTITY SCALE NO.		DISTANCE (RECIPROCAL) SCALE NO.		MOLECULAR WEIGHT SCALE NO.		PROCESS PENALTIES SCALE NO.		CHEMICAL EXPOSURE INDEX

Identification of Containment Vessels being evaluated:

Name or Number (See Notes 2&3)	I.	II.	III.	IV.	V.	VI. (CEI)
Source #1 ____________						
To (1) Public						
(2) Other in-company Facility						
(3) Non-company Plant or Business						
Source #2 (if needed) ________						
To (1) Public						
(2) Other in-company Facility						
(3) Non-company Plant or Business						

NOTE 1 - The distance scale number in column III is the only factor normally expected to change, so col. III and the corresponding CEI (col. VI) are all that would normally be expected to differ from the first calculation for each source.

NOTE 2 - Only different sources of the same chemical should be evaluated on this sheet. Use separate Chemical Exposure Index & CEI Summary Sheets for each different chemical.

NOTE 3 - Use additional sheets if additional sources with differing potential impact are present.
NOTE 4 - It is important to document the worst case scenarios for future reference. See review procedure.

DEFINITIONS OF SCALE NUMBERS

I. Acute Health Hazard - The acute health hazard is affected by both the concentration at which a material is acutely toxic and the vapor pressure which creates the driving force to volatilize and maintain the material in the atmosphere. For purposes of this scale number, the Emergency Exposure Planning Guide (EEPG) in parts per million is used as the toxicity measurement. Volatility is measured by the vapor pressure in mm Hg. @ $25^{o}C$ up to a maximum of 760. An acute health hazard factor is determined by multiplying the EEPG concentration by 760 and dividing by the vapor pressure. The acute health hazard factors have been assigned scale numbers according to the following ranges.

5 = 0 - .99 Health Hazard Factor
4 = 1 - 9.9 "
3 = 10 - 99 "
2 = 100 - 999 Health Hazard Factor
1 = 1000 - 100,000 "
0 = > 100,000 "

The scale number as a function of EEPG and vapor pressure may also be seen graphically on Figure 1. Table I illustrates a number of materials. properties and scale numbers.

II. Vapor Quantity - Select the maximum weight of material which would be released as a gas, or would vaporized, during 15 minutes of the "worst case" situation possible. Select the worst case of pressure, temperature, mechanical failure, runaway reactions, contamination, or human failure that is possible, but do not arbitrarily assume 100% of the containment would be released and vaporized in 15 minutes. See Apprendix II.

4 = > 10,000 lbs. (4500 kg)
3 = 1000 - 10,000 lbs. (450-4500 kg.)
2 = 100 - 1000 lbs. (45-450 kg.)
1 = 10 - 100 lbs. (4.5 - 45kg.)
0 = < 10 lbs. (<4.5 kg.)

III. Distance - The distance between the point of release and (1) the public, (2) other in-company plants, and (3) other businesses. Public is defined as residences, collecting points of people (schools, churches, shopping centers, hotels, or frequently used public roads.

4 = < 1000 ft. (<300 m)
3 = 1000 - 5280 ft. (300-1600m)
2 = 1 mile - 5 miles (1.6-8 km.)
1 = 5 miles - 15 miles (8-24 km)
0 = > 15 miles (>24 km.)

IV. Molecular Weight - The density of the vapor is directly related to the molecular weight and inversely affects the rate of dispersion. (Note: in both distance and dispersion ratings, nonlinear or logarithmic functions have been ignored since absolute numbers are not the objective).

4 = > 45 molecular weight
3 = 34 - 45
2 = 23 - 33
1 = 15 - 22
0 = < 15

V. Process Penalties - The two largest driving forces in generating large amounts of vapor in short periods of time are (1) pressure or overpressure (e.g., liquids well above their boiling points or high pressure gases) or (2) runaway reactions. Therefore, if either condition exists, a penalty is applied. If the pressure on the system is over 10 psig (70KPa guage), use 2 for this factor. If the material is, or can become, thermally unstable below 100°C, or is reactive with common materials like air, water, or other possible contaminants, use 2 for this factor. If both factors apply, use 4. If neither apply, use 1.

REVIEW PROCEDURE AND CHECKLIST

1. Any plant or facility which requires a further review should notify the site Loss Prevention contact, furnish a copy of this Chemical Exposure Index, and agree to an appropriate review date.

2. At least one week before the review, a Review Package should be sent to each member of the review committee. (These names will be furnished after the review is scheduled.)

3. The Review Package should contain:
   A. A simplified process flowsheet showing containment vessels and quantity.

   B. A chemistry sheet (both desired and undesired reactions).

   C. A plot plan and area map marked with 3 circles, the radii of which equals the distances 1, 10, and 100 times the EEPG concentrations which would result from the quantity that could be released. Contact your Process Engineering group for assistance with the appropriate gas dispersion calculations.

   D. Show all gas monitors, spill detectors, or other devices to detect a release and list test methods and frequency.

   E. List plant responses to "worst case" loss of containment. Note: Items D & E should be week documented for future reference.

   F. List methods of communicating with those in areas which could be affected.

   G. List special things which have been done to minimize the impact, e.g., dispersion prediction systems in use, direct line to local law enforcement, community education programs, practice drills, etc.

   H. Submit a completed Containment and Compliance Checklist.

4. At the review, the site review representative will collect recommendations and furnish these in a letter.

5. Your response, plans, or actions should be reported to the representative within 30 days and maintained with your Chemical Exposure Index.

CONTAINMENT AND COMPLIANCE CHECKLIST

This checklist will assist the Review Committees in evaluating Credit Factors for the things done to prevent, detect, or control "Loss of Containment". Please "check" those that are complete, operational, or in compliance with known company rules, guidelines or requirements. Please be prepared to cover these and any other specific safeguards designed to reduce the related risk. Any item that cannot be checked should be marked with the percentage of completion. Mark N.A. if not applicable.

Complete Risk Reducing Credits

________ 1. All pressure vessel and relief device systems properly registered and inspections up to date. (No expansion joints or glass devices).

________ 2. Adequate Emergency Block Valves in place, remotely or automatically operated, and regularly tested.

________ 3. All operational controls and systems designed and routinely tested to "fail-safe".

________ 4. Critical Instrument Program up to date (e.g., redundant high level and temp. alarms, shut-downs, etc.)

________ 5. Operating Discipline complete and up to date.

________ 6. Vapor Detectors properly placed and tested regularly.

________ 7. Appropriate engineering specifications properly applied (e.g., lethal service, welded fittings, etc.)

________ 8. Are relief vents on toxic containers designed to minimize atmospheric emissions? How? (circle) Scrubber, Flare, or ______________________________.

________ 9. Failure analysis and nondestructive testing carried out where needed (e.g., X-Ray, vibration analysis or monitoring, acoustical emission, piping flexibility analysis - hot and cold).

________ 10. Physical barriers in place (for traffic, cranes, etc.).

________ 11. Overdesigned for excess pressure, if needed (e.g., pipelines in certain areas, tank cars, trucks, etc.).

________ 12. All personnel properly trained to understand hazards and emergency responses.

________ 13. Emergency Procedures (relating to this exposure potential) in place and annual drill held.

________ 14. Safety Rules and Safety Standards regularly reviewed and enforced.

________ 15. Loss Prevention Principles and Minimum Requirements appropriately applied.

________ 16. Tech Center Guidelines appropriately incorporated.

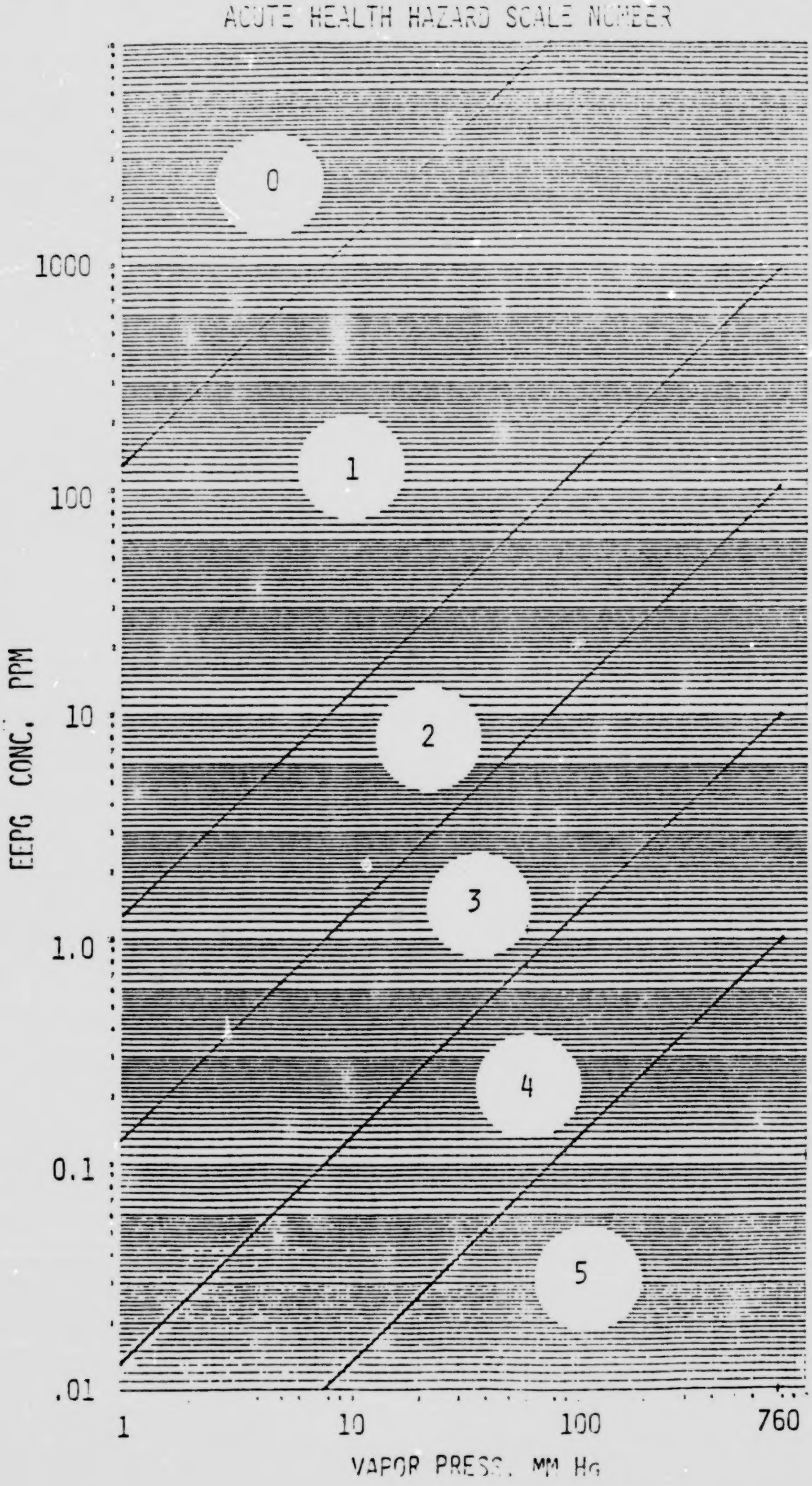
________ 17. Reactive Chemical Review within 2 years.

________ 18. Loss Prevention Audit within 2 years.

________ 19. Tech Center Audit within 2 years.

________ 20. All new operations and modifications underwent safety pre-startup audit.

FIGURE 1


ACUTE HEALTH HAZARD SCALE NUMBER
0
1
2
3
4
5
1000
100
10
1.0
0.1
.01
EEPG CONC., PPM
1
10
100
760
VAPOR PRESS., MM Hg

APPENDIX I

DOW EMERGENCY EXPOSURE PLANNING GUIDELINES (EEPGs)

Material	EEPG (ppm)
Acetone Cyanohydrin	10*
Acrylonitrile	20*
Allyl Chloride	25
Ammonia	100
Bromine	1
1,3-Butadiene	50
n-Butylisocyanate	0.2
Carbon Tetrachloride	100
Chlorine	3
Chloracetyl Chloride	1*
Chloroform	100
Chloropicrin	0.2
Ethyl Chloride	5000
Ethylene Dichloride	100
Ethylene Oxide	50
Formaldehyde	5
Hydrogen Bromide	5
Hydrogen Chloride	25
Hydrogen Cyanide	10*
Hydrogen Fluoride	10
Hydrogen Sulfide	20
Methacrylonitrile	10*
Phosgene	0.2
Propylene Oxide	500
Styrene	200
Sulfur Dioxide	10
Sulfuryl Fluoride	150
Toluene Diisocyanate	0.2
Vinyl Chloride	1000
Vinylidene Chloride	50

(*Avoid skin contact. This material is highly toxic by dermal absorption.)

An Emergency Exposure Planning Guideline (EEPG) is defined as the maximum airborne concentration of a material which, it is believed, nearly all individuals could tolerate for about one hour without incurring permanent health effects or symptoms which would interfere with their ability to take appropriate action.

These guidelines are intended to be used as a planning tool in the CEI process to determine priority concerns, to evaluate the adequacy of containment, to identify downwind areas which might need to take action during a release and to develop community emergency response plans. The need for an EEPG is based on the volatility of a chemical, its toxicity, the releasable quantity and the public's perception of the potential hazard.

The Organization Resource Council (ORC) is developing EEPG's for other chemicals in conjunction with major chemical companies under the auspices of the American Industrial Hygiene Association (A.I.H.A.).

Users should consult Industrial Hygiene specialists for specific information on other chemicals.

TABLE I - EXAMPLES OF ACUTE HEALTH HAZARD CALCULATIONS

CHEMICAL	EMERGENCY EXPOSURE PLANNING GUIDELINES (EEPG)	MOLECULAR WEIGHT	VAPOR PRES. MM HG @ 25°C	$\frac{760}{\text{VAPOR PRES.}}$	HEALTH* HAZARD FACTOR	ACUTE HEALTH HAZARD SCALE NUMBER (PLACE IN COLUMN I)
Phosgene	0.2	99.	Gas	1	0.2	5
Toluene Diisocyanate	0.2	174.	0.01	76,000	15,200.	1
Chlorine	3.	71.	Gas	1	3.	4
Hydrogen Cyanide	10.	27.	760.	1	10.	3
Sulfur Dioxide	10.	64.	Gas	1	10.	3
Hydrogen Chloride (Anhy.)	25.	36.5	Gas	1	25.	3
Ammonia	100.	17.	Gas	1	100.	2
Acrylonitrile	20.	53.	111.	6.85	137.	2
Ethylene Dichloride	100.	99.	87.	8.74	874.	2
Acetone Cyanohydrin	10.	85.	2.	380	3800.	1**
Bromine	1.	160.	223.	3.40	3.4	4
Hydrogen Bromide	5.	81.	Gas	1	5.	4
Chloroacetyl Chloride	1.	113.	25	30	30.	3

*Health Hazard Factor equals $\frac{\text{EEPG X 760}}{\text{Vapor Pressure}}$

**Dissociates to HCN on heating.

APPENDIX I

SCENARIOS FOR ESTIMATION OF RELEASE RATES FOR CALCULATING THE CHEMICAL EXPOSURE INDEX

All Dow manufacturing plants will be participating in ongoing reviews of the Chemical Exposure Index (CEI) for their plants. The CEI provides a guideline to the severity of possible releases of toxic vapors from various plants.

While catastrophic failure cannot be ruled out, and must be considered in emergency planning, the main intent is to use credible scenarios. (See rates in text).

Two factors to be considered when calculating the CEI are:

(1) A credible scenario for a release.

(2) The rate at which toxic material would be released in such a scenario.

When these two factors are considered together, it is possible to quantify a possible release rate.

Credible Scenarios

CEI's should be based on a realistic worst case, not the absolute worst case that could conceivably happen. It is suggested that the following definition of credibility be used, based on a workshop on Risk Assessment presented by Jerry Schroy of Monsanto in Boston in August, 1986:

> "A credible event is any accident for which a method can be defined which avoids the release of the chemical of concern to the atmosphere."

This definition discredits releases caused by unpredictable natural disasters, such as tornadoes, or manmade disasters such as an airplane striking a storage tank. It would also discredit releases caused by the simultaneous occurrence of two or more independent, improbable events.

It has been concluded by many people in the field of Safety and Loss Prevention that catastrophic failures are generally the result of an unlikely chain of events that are impossible to predict. In addition, release size estimation and dispersion calculations would be of minimal utility in the event of a catastrophic event. If a large release were to occur as a result of a complete tank failure of a hazardous chemical, it would be immediately obvious to the operators that the community should be notified. Complete tank failure is generally not a credible scenario since it almost never happens unless there is a fire or explosion. In such cases, products of combustion may have to be considered.

Following are some criteria for credible, worst case scenarios:

1. If a gasket failure occurs, the area between two adjacent bolts on the flange would blow out. Although smaller leaks occur, they are not serious enough to be a worst case. In the chemical process industry the number of bolts on a pipe flange are multiples of four. The exact number depends on the flange diameter and pressure rating. Asbestos or similar gaskets will blow out if they fail. However, after the section between two bolts blows out, the pressure in the pipe is reduced so that additional sections will not blow out. Teflon envelope gaskets do not blow out; instead, they develop small leaks which can increase in size significantly. Spiral wound gaskets do not blow out but can develop small leaks. The choice of area between adjacent bolts on the flange is

reasonable for gasket failure of asbestos or similar type gaskets. With spiral wound gaskets the leak rate would be considerably less, but unless there is assurance that maintenance people will not inadvertently install asbestos-type gaskets, it is probably desirable to assume they will be used. Gasket failures are not limited to any pipe size or flange rating.

2. Conclusions on holes in pipes and pipe breaks are based upon the recommendations of Brasie[1]. A two inch (5 cm) diameter pipe could break completely. However, if a hole were to develop in a pipe or vessel, the area of the break would not exceed two square inches (13 sq. cm). Complete pipe breakes are unreasonable for pipes over two inches (5 cm) in diameter. An unrealistically large force is needed to create a larger hole in a pipe or break a pipe larger than this.
3. Leaks at valve and pump seals are relatively frequent. Due to the mechanical complexity of these devices, these leaks are treated as a pipe leak of comparable area. It is assumed that leaks cannot exceed two square inches (13 sq. cm) in area from these types of equipment.
4. If it is reasonably possible for a valve on the end of a pipe to be fully open and release the contents of the pipe plus, for example, a tank, this could be a credible worst case, but it would also suggest some redesign of the system.
5. Calculations of credible releases from relief valves or frangibles exist as part of current design practices for relief devices. The design calculations for all relief devices used by The Dow Chemical Company are based on a code requirements. These design specifications, including the design release amounts, should be kept by each plant. Older plants should have relief devices checked for compliance with latest code requirements.
6. Tank overflows and spills of chemicals are credible, as long as they are the result of single malfunction. Thus, a tank overflow caused by a faulty level indicator is credible, while an overflow caused by both a faulty level indicator and malfunctioning pump is not. A hole in a tank not exceeding two square inches (13 sq. cm) in area is credible; larger holes are not credible.

IN SUMMARY:

Credible leaks include:

1. Gasket failures
2. Holes in pipes and pipe breaks; holes in vessels
3. Pump seals
4. Valves at end of pipes
5. Releases from safety devices
6. Overflow from tanks

Non-Credible leaks include:

1. Failures of entire tank
2. Massive failures of vessels
3. Pipes of greater than 2 in. (5 cm) diameter breaking completely

Reference

(1) Brasie, William C, "Guidelines for Estimating the Hazard Potential of Chemicals", LOSS PREVENTION VOL. 10, A CEP Manual, AIChE, New York, 1977.

THE HIDDEN PROBLEMS WITHIN EMERGENCY SITE MANAGEMENT

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INTRODUCTION:

We have prepared this paper in the hope that we may be able to assist future emergency site response personnel to recognize and cope with the hidden problems associated with Emergency Site Management.

We will not assume that all readers of this paper are familiar with the term Emergency Site Management. Therefore, we will first briefly describe Emergency Site Management, including the on-site procedures that are now being used as they relate to a chemical spill.

EMERGENCY SITE MANAGEMENT is a process that an emergency response agency uses to change a dangerous or potentially dangerous uncontrolled incident into a safe and controlled environment.

In order for the process to be successful, the Emergency Site Manager (E.S.M.) must be able to establish and communicate his objectives with all agencies involved at the emergency site, and should consider the following:

Initial Risk Assessment:

At the initial response stage to an emergency incident, it is imperative to identify all hazards considering the potential to life, property and the environment. The Emergency Site Manager must make immediate observations and gather all available information in order to make the best possible assessment at this stage. This can be done through vehicle placards, container type and labels, shipping documents, contact with the shipper and carrier.

Two very important factors that must first be considered at this initial stage are weather (i.e. wind direction - face the site with the wind at your back) and the geographical location (i.e. lay of the land - which way will spilled product flow?). These factors, as well as other variables such as road and traffic conditions will determine the safest approach to the site.

The E.S.M. must now determine the hazards and potential risk factors such as explosions, chemical exposures and fire (other considerations may include the possibility of building structure collapse - the additional variables depend on the given situation).

An initial casualty assessment may possibily be conducted at this point (depending on the risk factors to others). This would include search and rescue and initial care for the casualties and deaths.

Initial Site Stabilization:

The E.S.M. must take action to secure the incident site. Having identified the hazards and assessing the initial risk, he must establish safe working zones and site security. Any urgent public safety actions should be taken at this point. These may include:

- road closures and diversion of traffic;
- warning signs, barricades, etc.;
- emergency safey informtion to the public;
- emergency evacuations of people, residences, etc. which are at immediate risk.

Stabilization Process:

The E.S.M., having initially stabilized the site, must co-ordinate the development of a safe "plan of operation" to solve the problem. In order to achieve this goal he may utilize the following process:

1. Establish an Emergency Headquarters (Command Post) in a safe zone.
2. Appoint a Site Safety Officer, a Security Officer, a Recording Officer Public Communication Officer and a Logistics Officer.
3. Establish proper communications.
4. Establish a staging area and routes for incoming and outgoing emergency and assistance vehicles.
5. Obtain medical assistance at the site, i.e. doctors, ambulances, etc.
6. Notify hospitals of casualties including type of possible chemical contamination.
7. Establish a media release system.
8. Establish hot zone (high hazard) and a decontamination area after gathering more information and completing a more thorough risk assessment (i.e. by entry personnel in full protective equipment).
9. Set-up think-tank (brain storming) sessions with all key players such as fire, police, ambulance and technical representatives, in order to "GATHER INFORMATION" and to formulate a safe "plan of operation", including possible alternatives.
10. Implementation and monitoring the "plan of operation".

Emergency Site Managers deal with people under stressful conditions which can result in a number of hidden problems for the managers. We will discuss two hidden problems that we have encountered at emergency sites. We describe them as hidden because they do not appear obvious until they are encountered.

HIDDEN PROBLEM #1

"Sense of Urgency Takes Over"

Emergency situations can be difficult to compare because of their inherent unique set of circumstances. In addition, they involve a cast of characters with various expertise and personalities which is never the same at any given site.

Despite this, through experience and communication, we can identify "common ground" and learn accordingly. Even though we are forced to describe a specific problem in general terms, its awareness may be helpful to others.

In order to explain the potential problem that we wish to make you aware of, you must imagine yourself in a Command Post "think-tank" meeting trying to come up with the best "plan of operation" to remedy the situation (previously referred to in point #9 of **Stabilization Process**). The Emergency Site Manager may handle this meeting in any given manner. Let us assume that the E.S.M. gathers the necessary resource people and conducts a meeting in which everyone is invited to contribute their information and ideas. All persons may be respectful of each other and an open minded atmosphere may prevail. However, the stressful nature of an emergency situation tends to cloud our perspective at that point. Time appears to be the enemy at this stage. Outside pressures continue to mount either consciously or unconsciously. Political and media pressures as well as the general public may be demanding a quick solution.

A sense of urgency seems to creep into the meeting. The feeling of "let's not just sit here - let's do something" tends to take over. It's not a panic situation, it's just an atmosphere that may prevail. The result is that a "plan of operation" may be derived in a rather hasty manner. Consequently it's success depends on good luck rather than good planning.

The Solution:

When an emergency situation has been initially stabilized it is important to realize that "time" is an asset and not your enemy at this stage. The Emergency Site Manager and the resource people must remind themselves of this fact. This awareness may help them use their time more effectively.

A successful plan must be thoroughly thought out anticipating needs and considering all the alternatives. A strong sense of urgency tends to hinder the creative and logical thought process required to best achieve such a plan.

The E.S.M. can help neutralize the pressure caused by the sense of urgency. This does not mean the seriousness and ramifications of the incident are ignored. It means that they must use a disciplined approach which will enable the situation to be looked at more objectively. The E.S.M. may accomplish this by establishing a minimum time period for a "think-tank" meeting. It should be explained that a "plan of operation" will not be implemented until the expiration of this time period even if they feel they have arrived at a plan sooner.

The plan should be clearly written out and include diagrams where applicable. A rehearsal or "paper exercise" should be conducted whereby all persons in the meeting are invited to constructively try to find faults with the plan. Major fault(s) may be discovered which would prohibit the implementation of such a plan. In such a case, a new plan would have to be derived and explored using the same technique.

This refining process, a disciplined approach, will enhance the likelihood of formulating the best "plan of operation". In so doing, it also provides a solution to the hidden problem by not letting the "sense of urgency" obstruct the objective though process required at an emergency situation.

HIDDEN PROBLEM #2

The 2nd hidden problem within EMERGENCY SITE MANAGEMENT that we have encountered is the lack of understanding of the concept of an EMERGENCY SITE MANAGER and his "Authority".

Emergency situations have become much more complex. This is due to the rapid increase in the number of different chemicals being transported in today's technical world as well as the greater media coverage and general awareness when emergency situations take place. Consequently, this has caused the gathering of numerous response and resource personnel at an Emergency site from various backgrounds who are quite often strangers to each other.

At a relatively small incident, for example, such as a chemical spill from an over-turned tanker-truck on a rural highway, we may find as many as 50 - 60 people involved. This may include;

> police, fire, ambulance, government agencies such as public safety services and environment, the media, emergency response teams from industry, other representatives of the consignor, transporter and consignee, equipment specialist, highway crew, tow truck operators as well as general logistic personnel.

The E.S.M. is the site controller and as such has the authority and overall responsibility for the site and all personnel on the site. The process of emergency site management will be seriously jeopordized if any agency operating on the emergency site fails to follow commands issued by the E.S.M. All responding personnel, both technical and emergency services, must be informed of who is in command and they must acknowledge and accept this authority.

Here in lies the hidden problem. Various response and resource personnel that attend emergency situations are not accurately aware of or understand the role of an Emergency Site Manager (this may include, in some cases, the E.S.M. himself). These people may have never encountered an emergency situation before and they may never come across one again. In addition, they may be unaccustomed in taking direction from someone other than their normal employer.

This lack of understanding can cause serious problems. An agency may assume that a command from the E.S.M. is actually a suggestion. Once outside the Command Post, they may decide not to follow what they thought was a suggestion and do something entirely different. This could seriously jeopardize the safety of all personnel who had followed the original command.

To add to the problem, an agency may not be familiar with a very assertive leadership style of an E.S.M. which is usually the case at the initial stage of an Emergency situation. Consequently, they may choose to be less co-operative and not participate within a team concept if required.

The Solution:

The Emergency Site Manager must know his role. He may not be the most knowledgable (technical expert) person pertaining to the products (i.e., chemicals) involved at the site. He is, however, the authority in command and as such will co-ordinate the gathering of information, review the appropriate advice and implement the "plan of operation".

The E.S.M. must ensure that his function is understood by all parties attending the scene (ideally, this should be incorported into disaster planning so that various agencies within a community are familiar with the process and therefore able to work harmoniously when called upon). His instructions must be clear and concise. He must have this understanding re-inforced with each agency upon arrival at the staging area so that they are aware that all procedures are established through the E.S.M. and must be strictly adhered to.

The possible reasons for departure from E.S.M.'s command may be the result of one or more of the following:

- E.S.M. does not understand his role
- E.S.M. instructions not clear and concise
- Agency not familiar with E.S.M. role
- Role of E.S.M. not re-inforced at staging area
- Very informal atmosphere and lack of structure at Command Post
- Agency not willing to co-operate

An E.S.M. should be trained in order to prevent the likelihood of the above noted pitfalls.

Should the E.S.M. recognize that his commands are not being followed, he must take immediate steps to correct the deviation. The E.S.M. may run across an agency that refuses to follow his commands. If this happens then the E.S.M. must insist that the police remove the obstructive personnel from the incident site.

Should the E.S.M. require the advice of the obstructive agency, he can then request that the agency send replacement personnel to the incident site.

Every emergency site will obviously involve a wide range of personalities and management styles within the E.S.M. position. However, the basic concept remains unchanged. An E.S.M. must understand the vital role that he assumes and ensure that others equally understand that role.

CONCLUSION:

We have identified two hidden problems that have been encountered at emergency incident sites. It should be recognized that other hidden problems may exist. We sincerely hope that the lessons learned from all incidents can be shared in an effort to maximize our ability to respond.

CANADA'S EMERGENCY RESPONSE SYSTEM

Mr. L.A. Swick
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Emergency Preparedness Canada

LADIES AND GENTLEMEN

As a starter, I must say that I am impressed with the selection of topics for this 5th Annual Seminar on Chemical Spills. To learn that there are so many initiatives and techniques for monitoring, containment, response and clean-up along with the personal skills to effect a wide range of countermeasures in a professional manner is reassuring to me as an individual and as an official responsible for public protection.

These technical capabilities coupled with other industrial endeavours, such as CAER[1]contribute to Canada's Emergency Response system. As such, I thought we might look at this system and Emergency Preparedness Canada's (EPC's) endeavours to ensure that it is uniform and effective through co-ordination and training. This overview of Canada's Emergency Response System will also provide you an opportunity to confirm your specific input and niche into the system.

In Canada, our approach to emergency preparedness and response is, I think, a very sensible one.

It is based on the premise of graduated response. The individual/industry is the first to respond to an emergency. If they can't cope, the local municipal government takes over. If help is required from surrounding municipalities, or from the provincial government, it is requested and provided, in accordance with a pre-arranged plan.

If the occurrence can't be managed with the resources within the province or territory, or if, by the nature of the emergency, it has federal or national implications, then at the request of a province or territory the resources of the federal government are brought to bear. A good example of how federal assistance to a province during a severe emergency is the Edmonton Tornado.

Between 2:55 p.m. and 4:05 p.m. on the afternoon of Friday, July 31 the eastern part of Edmonton and parts of the counties of Strathcona and Leduc experienced severe winds, rain and tornado. Twenty-seven people were killed, and approximately 200 hospitalized because of injuries. Property damage in excess of $330 million was incurred, mostly in the areas of Sherwood Industrial Park, Clareview and Evergreen Trailer Park. Approximately 60 houses and 250 trailer homes were destroyed, 300 more houses were damaged. Two hundred businesses were destroyed or damaged. Over 3,000 jobs were affected with a possibility of 1,500 jobs lost for an indefinite period.

Usually, the federal government waits for a request from a province before offering assistance in disasters that cause property damage, as these normally fall within provincial jurisdiction. But in this case, the damage caused by the tornado was so great that the federal government wasted no time and responded immediately. Jim Hoffman, Regional Director of Emergency Preparedness Canada for Alberta and Northwest Territories contacted the Alberta Public Safety Services to indicate the federal government was standing right beside Albertans. So the Edmonton Tornado was unique in that all three orders of government were involved from the beginning.

As the city of Edmonton and the counties affected began rescue operations, the Atmospheric Environment Services of Environment Canada continued to provide weather information, the Department of National Defence placed helicopters and ambulances on standby and at the disposal of the provincial and municipal officials and Transport Canada's CANUTEC assisted in dangerous goods response.

On-site federal actions were co-ordinated by the Regional Director EPC, Alberta. Numerous federal departments and Crown corporations played a part in post-disaster recovery. They included Canada Post, the Department of National Defence, Consumer and Corporate Affairs, Health and Welfare, Employment and Immigration, Regional Industrial Expansion, and Canada Mortgage and Housing Corporation.

For those of you who have ever been part of a response to a serious incident where the public is under severe stress, you will value the activity of "co-ordination." The handling of displaced persons, casualties, and the recovery program is a complex piece of administrative machinery. The ability to access federal advice and assistance through one point of contact really facilitates coordination and the whole recovery process. This one window approach to federal assistance is a key aspect of the EPC function.

EPC also participated in the establishment of what we refer to as "one-stop victim assistance centres" which involved all three orders of government, the Insurance Bureau of Canada, and volunteer agencies. These Centres registered losses and damage, assisted with housing needs, provided immediate clothing, food and emergency financial assistance, and arranged distribution of various federal payments such as family allowance, unemployment insurance and old age pensions, as well as unemployment insurance registration. Insurance company representatives at these Centres arranged for advances on claims. In addition to playing a key role in the immediate disaster response, the Centres also laid the groundwork for the personal counselling and services that disaster survivors would need for some time to come.

Imagine the counselling, the consoling and individual care required in this specific case. Here is an extract of an article on the tornado which appeared in a recent issue of the EPC Digest[2]. Incidentally, many of my references to the Edmonton Tornado are based on this same article by Joan Borsu of our Public Information Division.

> "One elderly woman, a resident of Evergreen Mobile Home Park, was overwhelmed by what had happened. She told a reporter that she had been right in the centre of the tornado, sitting in her wheelchair utterly helpless. She looked out the window just in time to see her son's trailer fly right up into the air, twist to one side, and blow away."

Undoubtedly, this would have been a traumatic experience. Healing the emotional cracks from such an experience is never easy. Incidentally, 15 of the 27 people killed were residents of the Evergreen Mobile Home Park.

From all reports, the federal assistance and response needs of victims of the Edmonton tornado worked well. WHY? Again, from the Digest, and I quote:

> "It was because of the interpersonal relationships different emergency planners from different levels of government and industry developed after sitting through so many emergency planning meetings. When we finally got into the room together we all felt a sense of collegiality. Knowing the faces around the table is an incredible advantage in an emergency - you knew you could really count on these people!"

This quotation confirms what we know; namely, planning and having detailed plans in place are the essential ingredients to an effective emergency response system. In the federal government, each department or agency must develop its own plans, within its own budget. The agency responsible for co-ordinating emergency planning in the various departments and agencies is Emergency Preparedness Canada.

For most emergencies, it is known in advance which federal department or agency will take the lead role in the federal government's response. For example, in air crashes it would be Transport Canada; in oil/chemical spills on lakes or rivers where the environment is at risk it would be Environment Canada.

In addition to co-ordinating federal plans, EPC has a general responsibility to make Canadians more aware of the need for emergency preparedness.

As part of this effort, we sponsor conferences, and at times are co-sponsors of conferences such as the November 1987 Meeting of MIACC. In addition, we administer federal programs designed to help provinces and municipalities to develop plans, and to train and equip staff. One of our main goals is to have in place adequate, uniform emergency response capability across Canada. We administer the Joint Emergency Preparedness Program. Six million a year is made available to provinces, and through provinces to municipalities, to help with projects that will enhance Canada's ability to respond to national emergencies. These projects include:

- Computer information system for Saskatchewan
- Chemical Suits for several municipalities
- Hazardous Materials Training for regions
- Command Post/Rescue Vehicles for several towns

Another EPC program is Disaster Financial Assistance Arrangements, (DFA) in which the Federal Government reimburses a province or territory for a portion of the expenditure it incurs in recovering from a major disaster. In the Alberta disaster, Mr. Mazankowski, Deputy Prime Minister, in his tour of the devastated Edmonton area, offered DFA and nominated the Regional Director, EPC as the federal co-ordinator and spokesman. The program also extended to the industrial sector so that business and the economy might be re-established quickly.

We are all aware of the importance of timely information and intelligence at time of crisis. As such, we also maintain a Situation Centre to collect and interpret emergencies. It has sophisticated communications equipment and receives reports continuously from across the country and from the news media. In the case of the Edmonton tornado, assessment reports of the damage were condensed into situation summaries for dissemination to the Prime Minister's Staff, Privy Council Office (PCO), Emergency Preparedness Canada Senior Staff, Minister Responsible for Emergency Preparedness, Canada Mortgage and Housing Corporation (CMHC), Health and Welfare Canada (H&WC), Employment and Immigration Canada (E&IC), Department of National Defence (DND) and other concerned federal departments.

Having exposed you to the federal support available to the provinces and the working arrangements, I would like to say a few words about our bilateral emergency planning with the United States.

As geographical neighbours and military allies, the two countries share many emergency related concerns, and have much to gain from a well-developed, co-operative relationship in emergency planning and management. EPC maintains regular contact with its counterpart organization in the United States, the Federal Emergency Management Agency (FEMA), to encourage and co-ordinate joint preparedness initiatives.

Traditionally, the Canadian and American governments have worked together in dealing with floods and forest fires. In 1986, in keeping with this tradition, an existing formal agreement was updated to ensure co-operation in all kinds of disasters ranging from drought to a nuclear attack on North America.

The centrepiece of the Agreement is a series of ten principles of co-operation, intended to establish a framework for the conclusion of future bilateral arrangements in the area of civil emergency planning.

Having given you a brief introduction to emergency preparedness arrangements in Canada and with the U.S., EPC's role in them, I should now like to deal in more detail with our training and research activities.

Today we conduct something like 17 courses with an annual put-through of 3500 students on a budget of some $2.5 million.

Current course offerings include one on Exercise Design. It provides the participant with the knowledge and techniques to design and conduct exercises tailor-made for his or her own municipality. We all know that a well-conceived and properly run exercise involves many sectors of the community in a positive way. Given good media exposure, an exercise helps the general public become aware of what is being done on their behalf to prepare for emergencies, and what they can do for themselves.

Another course, Emergency Operations, enables planners and officials to operate effectively as staff members of an Emergency Operations Centre (EOC). The course covers principles of operations and control, and introduces standard operating procedures to be applied in EOC as well as the practical aspects of organizing and exercising EOCs. The Mayor of Mississauga, shortly before the train derailment (November 10, 1979) had attended such a course. Consequently, she had a good knowledge of how to effect command and control particularly with respect to the difficult phase of public evacuation.

There is a Transportation of Dangerous Goods Course directed at the training of emergency response personnel who would deal with a transportation accident where dangerous goods are involved.

The School offers an Emergency Site Management Course designed to enhance the candidate's ability to direct, control and cooordinate operations at an emergency site. This course is management-oriented. It is not a basic skills course. It aims at improving the awareness, management co-ordination and the planning needed by emergency team leaders. Participants are exposed to the essential information necessary to prepare them to work effectively as part of and/or manage a group of emergency response teams.

The Site Management Course was developed at the request of the provinces. In December of last year, we received a letter which emphasized the value of this course. To quote:

> "As the Fire Chief and Assistant Director of Disaster Services for a municipality that was hit by the Edmonton Tornado, I would recommend this course to other senior fire, police and emergency medical personnel."

Here are some other courses offered at the College:

- Plans and Operations (Peace and War)
- Mayors and Elected Officials - Emergency Readiness
- Radiological Defence Officers' Course
- Fisheries Emergency Operations
- Community Emergency Services
- Analysis and Design Fallout Protection

In order to be able to employ the latest teaching techniques at the College, we have installed a state-of-the-art audio-visual system. This permits us to stage, for example, interactive simulated exercises, including realistic news conferences. We also have available closed-circuit television, and are developing computer-assisted training as well as considering distance education, using satellites.

The majority of the courses are conducted at the Canadian Emergency Preparedness College, which is located on a 35-acre campus outside Arnprior near Ottawa. All of the courses are offered free of charge to the participants, and EPC pays for the accommodation and travel of those students selected to attend.

In support of our training program, we also carry out and sponsor some research. For example, we have learned much from "first-response" studies carried out by a multi-disciplinary team from Carleton University. This team, which has been investigating disasters for some twelve years now, is led by Professor Joe Scanlon from the faculty of Journalism, University of Ottawa. By using network observation techniques, survey tools, and interviews, the research team has documented a number of disasters ranging from air crashes to chemical spills. The accumulated knowledge has led to interesting comparative studies in which communications difficulties, emergency operations and co-ordination, and adequacy of planning have all been assessed.

We have been doing some computer studies on wind patterns and radioactive fallout predictions. The results can be incorporated into exercises to demonstrate realistically the difficulties planners and disaster managers face in preparing for the worst situation; namely war.

We assisted the University of Manitoba in the development of a chemical plume forecasting model. Today there are some sophisticated models in place. I'm not sure how the Manitoba initiative would stack up against NOAA's Cameo.

Another project which we support is HERMES (Heuristic Emergency Response Management Expert System). This undertaking is being pursued by the Alberta Research Council and was addressed earlier by Dr. Chang.

Much of our training is developed with considerable input from the provinces and life-saving services. We must capture such expertise in course development. In this connection, a Basic Awareness Training Program for those first on the scene of a Transportation Dangerous Good (TDG) accident has been prepared, with notable effort by Alberta, and distributed to all of the provinces for their implementation.

We have also made considerable progress on the development of a "Hands-On Training Program for First Responders". This program will concentrate on the use of equipment and application of first-aid mitigation measures at a Transportation Dangerous Goods incident. The fire fighting community has been invited to comment on this training package.

To ensure that our training is as good as we can make it, we must continually assess how we are doing. To that end, we have recently developed and introduced a new course evaluation system at the College. As well, we are making greater use of statistical analysis to help us determine what we should be teaching and to whom.

As I approach the end of this presentation, I would like to say a few words about some new legislation. A recent development that should enable us to do a better job for Canada in the field of emergency planning, was the introduction by the government in June 1987, of two pieces of legislation, the Emergencies Act (Bill C-77) and the Emergency Preparedness Act (Bill C-76). The former mentioned, provides a new, improved and fully safeguarded legislative framework for response to national emergencies. It replaces the War Measures Act which has been subject to much criticism. The Emergency Preparedness Act clarifies responsibilities for civil emergency preparedness and establishes the role and mandate of EPC as a independent agency to co-ordinate federal emergency planning and to report to Parliament on the status of this planning. Following second reading, both pieces of legislation are under committee review.

To sum up, Emergency Preparedness Canada is the federal agency that co-ordinates, stimulates and facilitates emergency readines in all parts of Canada. In carrying out this role, we employ communication and participation, financial encouragement, and particularly training and associated research. We have some legislation which provides a platform for these initiatives.

Now, I would like to close on a congratulatory note. Over the past few years planners, researchers, operators, managers engaged in emergency activities have cried out for comprehensive, integrated and multi-disciplined approaches to research and response. Thanks to this seminar, we're doing just that.

(1) Community Awareness and Emergency Response

(2) Emergency Preparedness Canada, Joan Borsu, Emergency Preparedness Digest, Number IV, Volume IV, Page 10, November-December 1987.

HERMES:
Heuristic Emergency Response Management Expert System

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Don Clark, *Alberta Public Safety Services*
Greg Sidebottom, *Alberta Research Council*

ABSTRACT

HERMES, a prototype expert system to provide advice and assistance in the management of emergencies involving hazardous materials, was developed by the Alberta Research Council, Alberta Public Safety Services, and Emergency Preparedness Canada. This system was implemented on the Symbolics artificial intelligence workstation, using the ART (Automated Reasoning Tool) software.

The system utilizes information entered by the user regarding the nature of the accident and the environmental variables to make estimates of hazard levels such as the risk of fire and explosion, to make recommendations about procedures to follow for containment and possible evacuation, and to decide on additional information that should be gathered. Information about the accident concerns the material(s) involved and the rate and volume of leakage; environmental variables include ambient weather conditions, proximity to population centres, topological and cultural features such as land slope, bodies of water, and nearby traffic movement.

HERMES was constructed using the knowledge in standard handbooks for emergency response management, as well as the experience of experts who work daily in managing these situations. It includes calculations for the dispersal plume and the area of recommended evacuation based on the distance of projectiles upon explosion and using the Gaussian plume equation for a mathematical model. A special feature in HERMES is the graphics/mouse-oriented user interface that permits variables to be updated conveniently so that rapidly changing situations are easily managed. Also, a tutorial mode is available to assist the trainee in making situation assessments and risk estimates, as well as in deciding the appropriate courses of actions to follow.

HERMES has been prototyped to produce general responses for only a few common hazardous materials involved primarily in surface transportation such as propane, liquid nitrogen and anhydrous ammonia. The technology of expert systems facilitated the development of the prototype and will permit its easy modification and adaptation to new materials, more complex situations and additional knowledge.

INTRODUCTION

Expert Systems technology continues to expand its area and variety of application; and vice versa, more and more people in different disciplines are accepting expert systems as a viable approach for solving their problems. Emergency response management is one such area that has realized the advantages that expert systems techniques may provide. Historically, agencies required to respond to dangerous goods incidents utilized libraries containing safety information for specific chemicals and more general references on response procedures. Information access could be tedious and experience was required to know which volumes to search. There usually was not one single source which could provide all the necessary information. It was realized that organizing the information into a data base such as the Dangerous Goods Information System (DGIS) developed by Alberta Public Safety Services (APSS) could resolve some of the problems presented by hard copy data. APSS and Emergency Preparedness Canada (EPC) believe that the next step to improved performance lies with expert systems which will aid not only in the organization and retrieval of information but also in a higher level of information processing with automated decision making. Consequently, the system HERMES (Heuristic Emergency Response Management Expert System) was developed, by APSS, EPC and the Alberta Research Council. It is a prototype expert system to provide advice and assistance in the management of emergencies involving hazardous materials.

Emergency response personnel dealing with a chemical spill situation usually enlist the assistance of experts in the domain of the problem for hazard assessment and countermeasure possibilities. In Alberta, this expert consultation is provided by the APSS Compliance Information Centre 24-hour hotline manned continuously by a group of experts working rotating shifts. A typical situation is an accident involving vehicles transporting dangerous goods. Police and firemen arrive at the scene of the incident and relay the information regarding the situation to the expert on duty at that time. Given the emergency description and using the computerized database (DGIS), hardcopy information and personal experience, the expert must determine the nature of the crisis and provide quick effective advice on how to best deal with the situation. These experts must consider the properties of the substance in question as well as the immediate and long term effects to populations and the environment. Even after the initial crisis situation has been controlled, any proposed cleanup procedures must minimize adverse environmental effects and consider cleanup costs.

The following main difficulties associated with the task of emergency response management have been noted.

- There is a large amount of information that must be searched, there are numerous factors that must be considered in assessing the situation and even experts may, especially in a crisis, miss some of them.
- The expert often deals with incomplete or inexact information and complicated by the fact that he is far removed from the scene of the accident, it may be difficult to quickly form decisions.
- In connection with the preceding point, the particular incident may be outside of the realm of the expert's particular experience or correct procedures may not be documented in the expert's resource materials. Thus, personnel with more varied or greater experience may have to be consulted or called in during silent hours. Delays such as this are more likely to occur when trainees are on duty.

Clearly, emergency response management is an area that could benefit from an expert system solution, and this study has been conducted to determine the feasibility of such a solution. The result of the study is HERMES, offering expert systems technology together with the ability to handle incomplete data, sophisticated interfacing modules, advising and tutoring functions as integral components of the solution.

THE EMERGENCY RESPONSE PROBLEM

The emergency response process involves two main forms of actions—immediate actions and post emergency actions. An immediate action or initial emergency response is concerned with substance identification, human safety, fire control and the containment of the spill. Post emergency actions include cleanup procedures and assessment of long term effects on the environment and human health. The primary task in emergency response management is to determine each of these actions according to the conditions of the situation.

Chemical identification should be available from the shipping documents, placards or labels on the container, or from the manufacturers and suppliers. Otherwise, other identifying

Table 1. RESPONSE CONSIDERATIONS

Factor	Description	Effect
purity	usually available with identifying information	on colour, odour, toxicity, etc.
physical state (solid, liquid, gas)	state of pure substance at 20°C and 1 atmosphere pressure is documented for most substances; state change with ambient conditions may be derived using some known mathematical expressions	affects toxicity, solubility, fire properties
solubility, vapour density, viscosity	recorded properties for most materials	effect on dispersion into environment
exposure limits	limits for inhalation, ingestion, contact with skin or eyes documented for most substances	determines human protection measures
fire, explosive limits	recorded properties for most materials	effect on flammability and explosion hazard
ambient weather conditions		affects properties of substances
leakage	solid, liquid or gas venting estimation based on puncture size and location, ambient temperature, pressure, mass, volume	determines flammability, environmental toxicity
dispersion	models are available for calculating behavior in air, water, soil, based on numerous properties of materials combined with ambient weather, proximity to population centres, land slope, bodies of water, nearby traffic	hazard to environment and human health
chemical compatibility	reaction with other materials documented for most substances	knowing potential problems with coreactants affects fire prevention, spill stoppage, cleanup procedures

characteristics such as colour, odour and container type may be considered. Upon identifying the substance, a manual [3] or a database is consulted for the corresponding hazard assessment and general responses. However, it is emphasized that only general information and advice are provided; every spill is different and a general guideline may be found to be inappropriate under specific circumstances. For example, in the case of a liquefied propane leak, an advice would be "Stop leak if without risk", but the response team must still use knowledge, experience and sound judgement to further determine that there is no risk. More concretely, the response team then faces a more involved task of considering the properties of the substance together with the specific conditions of the spill situation [4]. Some of these factors and corresponding effects on a spill situation are summarized in Table 1. Not included in this table are other less common factors but which could equally complicate the situation such as economic and political issues. And then there are also the secondary tasks of minimizing operation costs, scheduling courses of action and scheduling resources such as manpower and equipment.

An important characteristic of the emergency response process is the generality if not the unavailability of input information. For example, the source of the leak may not be in view so that it is not possible to provide the response team with the size of the puncture. However, it is interesting to note that for every little information about the incident that becomes available, the expert is able to generate some relevant advice although sometimes it is necessarily conservative and over cautious.

HERMES: AN EXPERT SYSTEM EXPERIMENT

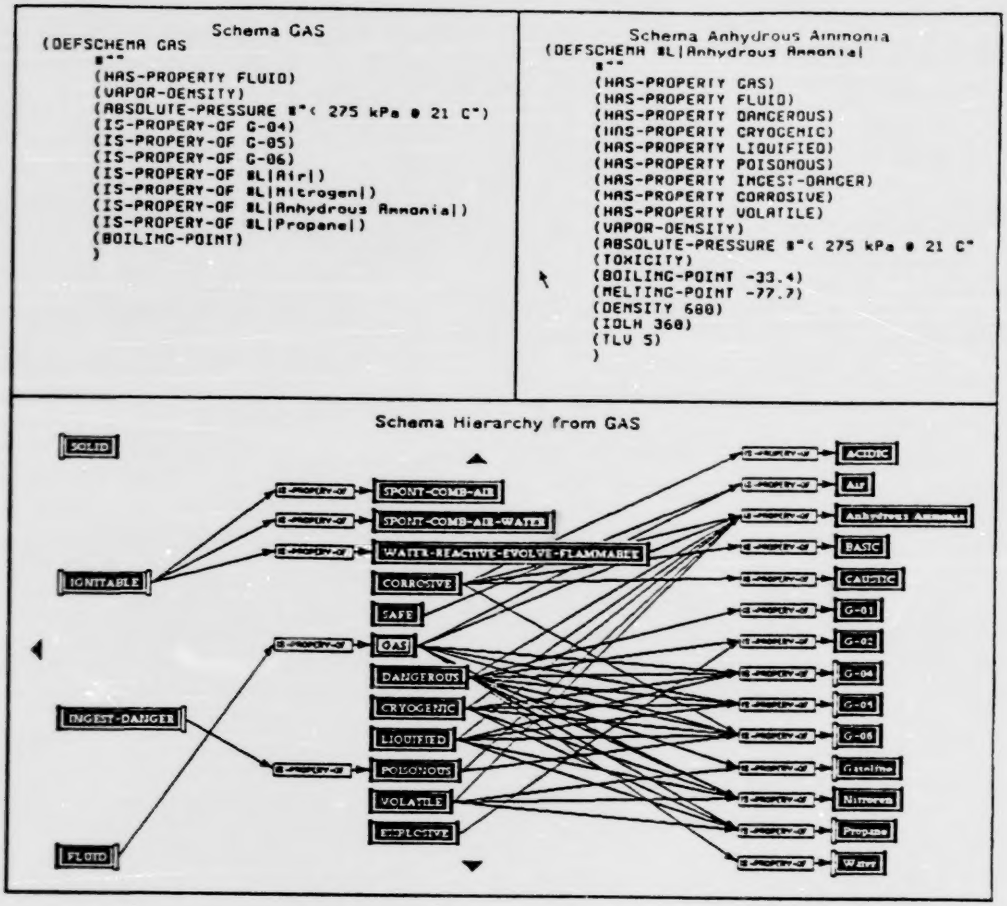
An expert system is described as "A computer system that achieves high levels of performance in task areas that, for human beings, require a (substantial amount) of special education and training", a system for which "knowledge provides the power for solving important problems" [1]. Knowledge is available as public knowledge which includes published definitions and theories in the domain of the problem, and private knowledge mainly composed of heuristics or "rules of thumb" in the sole possession of the human expert. It is heuristics that allow the expert system, like the human expert, to make educated guesses and handle inexact or incomplete information. With the preceding description of the emergency response problem, it is easily seen that emergency response management is a good domain for the application of expert system technology.

Some expert system experiments have already been conducted in the area of emergency response management. An early experiment involved crisis management at Oak Ridge National Laboratory (ORNL) where teams of expert system developers were set against each other to solve best the problem with several different expert system tools [1]. ORNL is a large research park having a complex network of sewage ducts, drainage basins and water sources where hazardous substances could seep. The problem was to allow a small off-hour staff quickly find and eliminate leaks of unknown substances. GEOTOX is a more recent work in the area of toxic substance management that evaluates disposal sites for hazardous wastes while taking into account substance properties, site conditions, economic factors and possible public reactions [5]. In each case, the potential of expert systems techniques as effective tools for large, real world problems has been realized.

HERMES is another experiment that takes advantage of the benefits of expert system technology. It is designed for a wider application of hazard evaluation and advice generation where most aspects of response processing, from leakage to environmental protection, are represented. The major features of HERMES are the use of knowledge representation techniques for representing both public and private knowledge, the sophisticated interfacing modules for ease of access to the represented knowledge, and the tutorial mode that enables the trainee to gain knowledge from the encoded experiences of the expert. With these functions and more, it is the goal of HERMES to be able to assist response personnel, whether experts or trainees, in the task of making effective, timely advice in the light of all variants, available or otherwise.

Knowledge Representation/Processing

Knowledge in HERMES is represented using a system of *frames* and *rules*. A frame, also known as a *schema*, corresponds to an object or idea in the world of the problem. Frames provide a natural representation for emergency response objects such as chemical substances and their properties. An object is described using a set of *attribute-value* pairs. Figure 1 gives examples of schemata for GAS and ANHYDROUS AMMONIA. Example attributes or *slots* for ANHYDROUS AMMONIA are DENSITY, BOILING-POINT and MELTING-POINT with values of 680, -33.4 and -77.7 respectively. A special type of slot is the *relation* that always has another frame for its value. Example relations in HERMES are IS-PROPERTY-OF and its inverse



Schema GAS

```
(DEFSCHEMA GAS
     #""
     (HAS-PROPERTY FLUID)
     (VAPOR-DENSITY)
     (ABSOLUTE-PRESSURE #"< 275 kPa @ 21 C")
     (IS-PROPERY-OF G-04)
     (IS-PROPERY-OF G-05)
     (IS-PROPERY-OF G-06)
     (IS-PROPERY-OF #L|Air|)
     (IS-PROPERY-OF #L|Nitrogen|)
     (IS-PROPERY-OF #L|Anhydrous Ammonia|)
     (IS-PROPERY-OF #L|Propane|)
     (BOILING-POINT)
     )
```

Schema Anhydrous Ammonia

```
(DEFSCHEMA #L|Anhydrous Ammonia|
     #""
     (HAS-PROPERTY GAS)
     (HAS-PROPERTY FLUID)
     (HAS-PROPERTY DANGEROUS)
     (HAS-PROPERTY CRYOGENIC)
     (HAS-PROPERTY LIQUIFIED)
     (HAS-PROPERTY POISONOUS)
     (HAS-PROPERTY INGEST-DANGER)
     (HAS-PROPERTY CORROSIVE)
     (HAS-PROPERTY VOLATILE)
     (VAPOR-DENSITY)
     (ABSOLUTE-PRESSURE #"< 275 kPa @ 21 C"
     (TOXICITY)
     (BOILING-POINT -33.4)
     (MELTING-POINT -77.7)
     (DENSITY 680)
     (IDLH 360)
     (TLV 5)
     )
```

Schema Hierarchy from GAS
SOLID
IGNITABLE
INGEST-DANGER
FLUID
IS-PROPERTY-OF
SPONT-COMB-AIR
SPONT-COMB-AIR-WATER
WATER-REACTIVE-EVOLVE-FLAMMABLE
CORROSIVE
SAFE
GAS
DANGEROUS
CRYOGENIC
LIQUIFIED
POISONOUS
VOLATILE
EXPLOSIVE
ACIDIC
Air
Anhydrous Ammonia
BASIC
CAUSTIC
G-01
G-02
G-04
G-05
G-06
Gasoline
Nitrogen
Propane
Water

Figure 1. Knowledge Base Structures in HERMES

relation HAS-PROPERTY. As shown in Figure 1, relations link schemata together to form hierarchies for classification and other ways of organizing knowledge. Hierarchies are characterized by a sharing of information which is made possible by *inheritance relations* that allow slots and values to be passed between linked frames. An example given in Figure 1 is ANHYDROUS AMMONIA inheriting from GAS the slot ABSOLUTE-PRESSURE and the corresponding value "< 275 kPa @ 21 C". Thus, this knowledge structure provides a system *default reasoning* in absence of information. However, it is important to note that inheritance can be overridden by, for instance, explicitly defining ANHYDROUS AMMONIA to have a boiling point of -33.4°C.

Rules represent knowledge that naturally translate into condition-action, premise-conclusion or if-then structures. In HERMES, theories such as the dispersal plume equation, and heuristics for determining emergency actions, are formulated into rules. The example rules below generate evacuation distance advice based on the characteristics of the substance and the fire type.

IF substance is gas
  substance is not flammable, not corrosive or not poisonous
  fire type is low intensity or high intensity
THEN
  set evacuation distance to 800.

IF substance is liquid
  substance is not flammable
  fire type is high intensity or impinging
THEN
  set evacuation distance to 300.

For the knowledge processing task, expert systems have separate control strategies for executing or *firing* rules to make inferences about the current problem presented by the input data. Inferencing involves either a *forward chaining* or *backward chaining* strategy. In forward chaining, rules with their conditions in the IF-part satisfied by input data are fired so that actions in the THEN-part are executed. This usually results in new information being generated such as for the evacuation distance in the example rules above. In HERMES, forward chaining is used primarily for generating advice. Backward chaining, on the other hand, is used to generate suggestions for input. Working backwards from the THEN-part to the IF-part, unsatisfied conditions determine the missing information. The user is then provided with the suggestion to fill in the missing details.

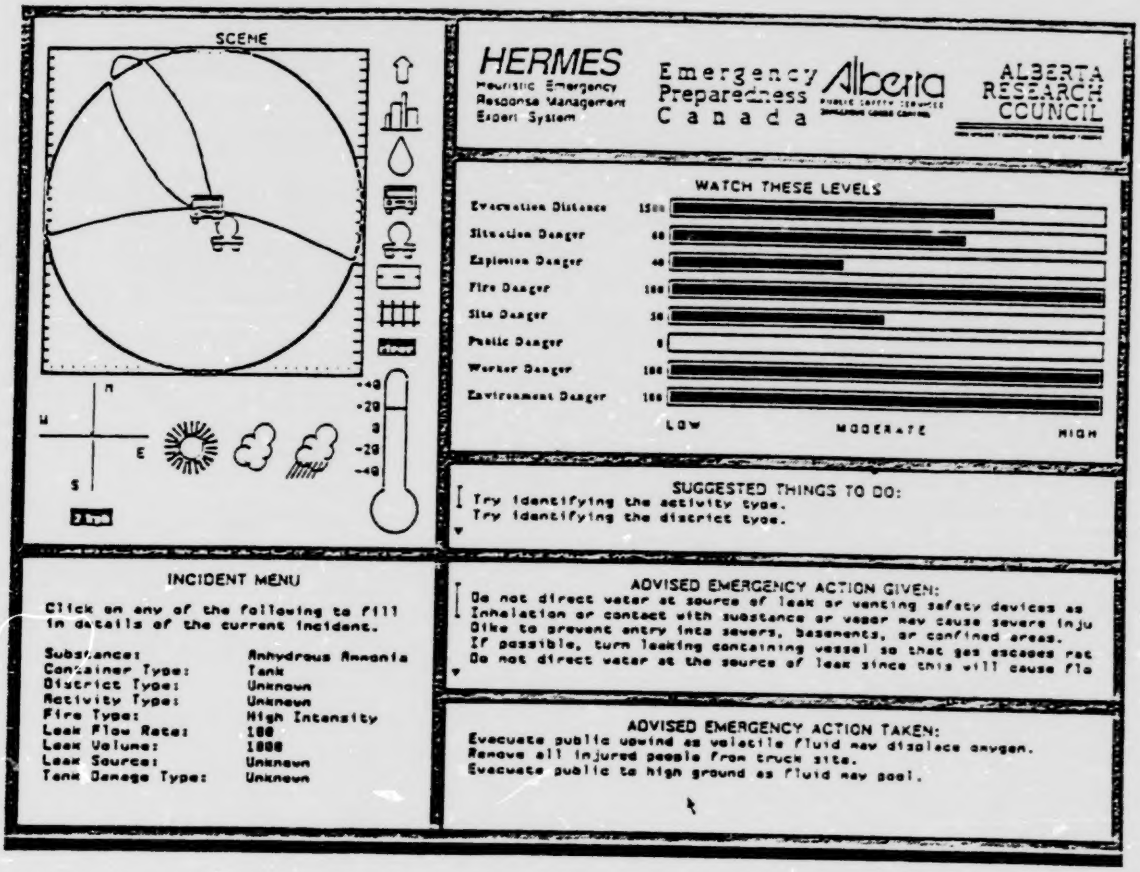
Aside from the rules and inference mechanisms, another control strategy for knowledge processing is the use of *procedural attachments.* These are procedures attached to certain slots of frames. The procedures are activated when the slots are accessed or the values are modified. The attached procedures, like the actions in rules, are usually used for producing new information. For example, in setting the value of the leak rate, a side-effect would be to assign a value to the leak volume.

As can be noted from the preceding discussion, data and control in expert systems are considered separately, making for ease of development and modification. This is the aspect of expert systems that HERMES aims to take advantage of while in the process of increasing the represented expertise.

The HERMES Interface

To facilitate the communication between HERMES and the human expert, the interface system of HERMES is designed with the following features (Figure 2):

- extensive use of graphics and the mouse
- facility to reconstruct the accident scene on a scaled 3-kilometer square canvas in the SCENE window; the user is able to place on this canvas objects such as trucks, trailers, roads, railway tracks, bodies of water, land slope and places where people are located
- facility to represent the weather conditions by using the mouse to click on icons in SCENE for the wind speed, wind direction, outlook and temperature
- facility for describing (by the user or HERMES) the substance, container, leakage and other incident details in the INCIDENT MENU window
- display of the evacuation limits (thick-bordered circle) and concentration area (thin-bordered oval) in the SCENE canvas
- SUGGESTED THINGS TO DO window to inform the user of areas which lack information; provides the user with the questions that may be asked of the person describing the accident



WATCH THESE LEVELS

Evacuation Distance	1500	
Situation Danger	60	
Explosion Danger	40	
Fire Danger	100	
Site Danger	50	
Public Danger	0	
Worker Danger	100	
Environment Danger	100	
	LOW	MODERATE	HIGH

SUGGESTED THINGS TO DO:

Try identifying the activity type.
Try identifying the district type.

INCIDENT MENU

Click on any of the following to fill in details of the current incident.

Substance:	Anhydrous Ammonia
Container Type:	Tank
District Type:	Unknown
Activity Type:	Unknown
Fire Type:	High Intensity
Leak Flow Rate:	100
Leak Volume:	1000
Leak Source:	Unknown
Tank Damage Type:	Unknown

ADVISED EMERGENCY ACTION GIVEN:

Do not direct water at source of leak or venting safety devices as
Inhalation or contact with substance or vapor may cause severe inju
Dike to prevent entry into sewers, basements, or confined areas.
If possible, turn leaking containing vessel so that gas escapes rat
Do not direct water at the source of leak since this will cause flo

ADVISED EMERGENCY ACTION TAKEN:

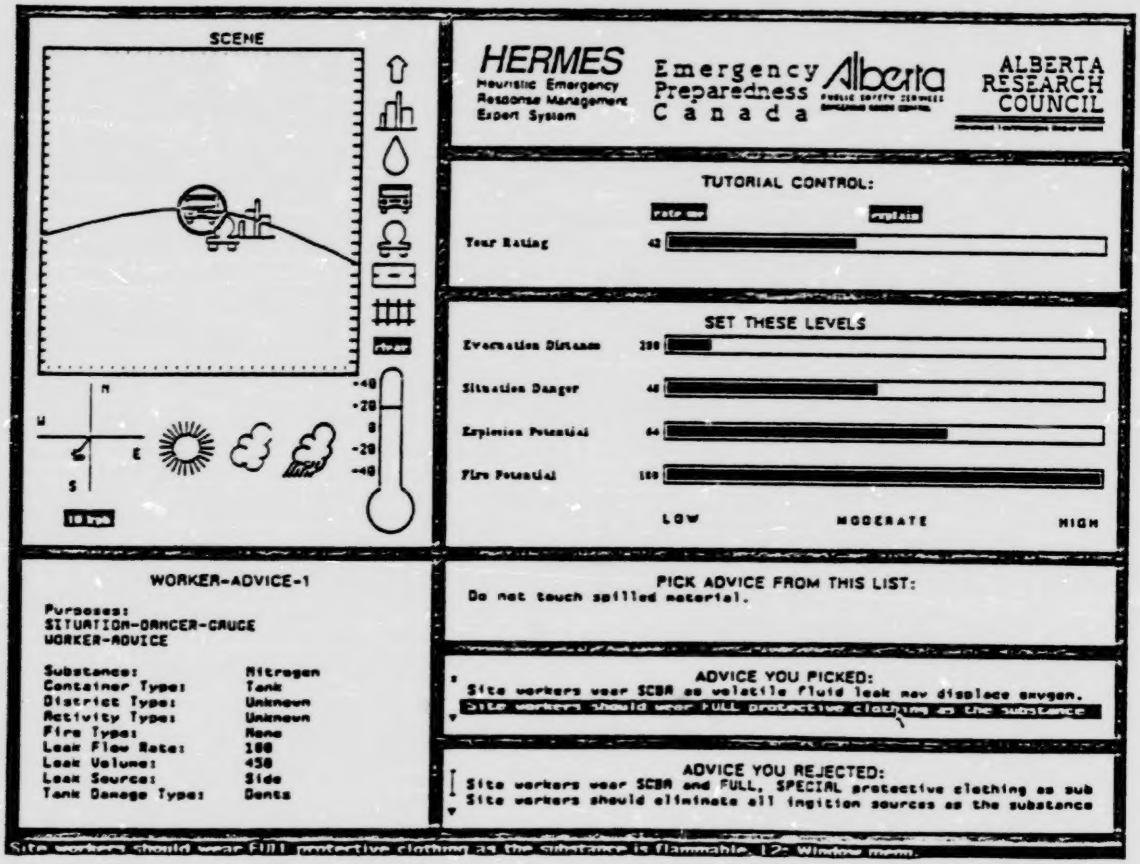
Evacuate public upwind as volatile fluid may displace oxygen.
Remove all injured people from truck site.
Evacuate public to high ground as fluid may pool.

Figure 2. The HERMES Expert System

- ADVISED EMERGENCY ACTION GIVEN window presenting a menu of generated advice; clicking the mouse on an advice transfers the chosen advice to the ADVISED EMERGENCY ACTION TAKEN window
- WATCH THESE LEVELS window presents hazard assessment results through gauges:
  - *evacuation danger gauge*: represents the minimum distance in meters from the accident site where the public will be safe from things such as explosion projectiles or hazardous atmospheres; the reading of this gauge is the radius of the evacuation area
  - *situation danger gauge*: indicates whether the situation involved is reasonably safe or is a major crisis; captures notions such as poisonous substances are more dangerous than flammable substances, leaks are more dangerous as the flow rate increases, and wind blowing from the site of a dangerous chemical leak towards a population center is worse than wind from the population to the leak
  - *explosion danger gauge*: estimates the explosion potential; the kinds of rules that increase the reading of this gauge are, for example, when there is an impinging fire on or gouges in a large compressed gas tank on a hot sunny day

- *fire danger gauge*: very similar to the explosion danger gauge; depends on things like the flammability of the substance and the existence of ignition sources
- the final group of four gauges: the *site danger gauge*, the *public danger gauge*, the *worker danger gauge*, and the *environment danger gauge*, are used to indicate how much of the advice has been taken care of; for instance, the reading on the worker danger gauge will decrease as the workers put on the correct protective clothing and start work to eliminate explosion hazards; finally, when all advice has been taken, these four gauges will have a reading of zero, correctly indicating that every suggested countermeasure has been carried out

- ability to adjust information displayed on the screen based on new or changing input information; screen editing procedures are attached to variables and are activated whenever a rule operates on these variables; for example, if the user resets the weather vane needle, a flood of activity takes place to ensure inferences the system makes are consistent with this new fact.


SCENE
clear
N
W
E
S
10 kph
+40
+20
0
-20
-40
HERMES
Heuristic Emergency
Response Management
Expert System
Emergency
Preparedness
Canada
Alberta
PUBLIC SAFETY SERVICES
ALBERTA
RESEARCH
COUNCIL
rate me
explain
LOW
MODERATE
HIGH

TUTORIAL CONTROL:

Your Rating 42

SET THESE LEVELS

Evacuation Distance 200

Situation Danger 48

Explosion Potential 64

Fire Potential 100

WORKER-ADVICE-1

Purposes:
SITUATION-DANGER-GAUGE
WORKER-ADVICE

Substance:	Nitrogen
Container Type:	Tank
District Type:	Unknown
Activity Type:	Unknown
Fire Type:	None
Leak Flow Rate:	100
Leak Volume:	450
Leak Source:	Side
Tank Damage Type:	Dents

PICK ADVICE FROM THIS LIST:
Do not touch spilled material.

ADVICE YOU PICKED:
Site workers wear SCBA as volatile fluid leak may displace oxygen.
Site workers should wear FULL protective clothing as the substance

ADVICE YOU REJECTED:
Site workers wear SCBA and FULL, SPECIAL protective clothing as sub
Site workers should eliminate all ingition sources as the substance

Site workers should wear FULL protective clothing as the substance is flammable. 12> Window menu.

Figure 3. The HERMES Tutorial System

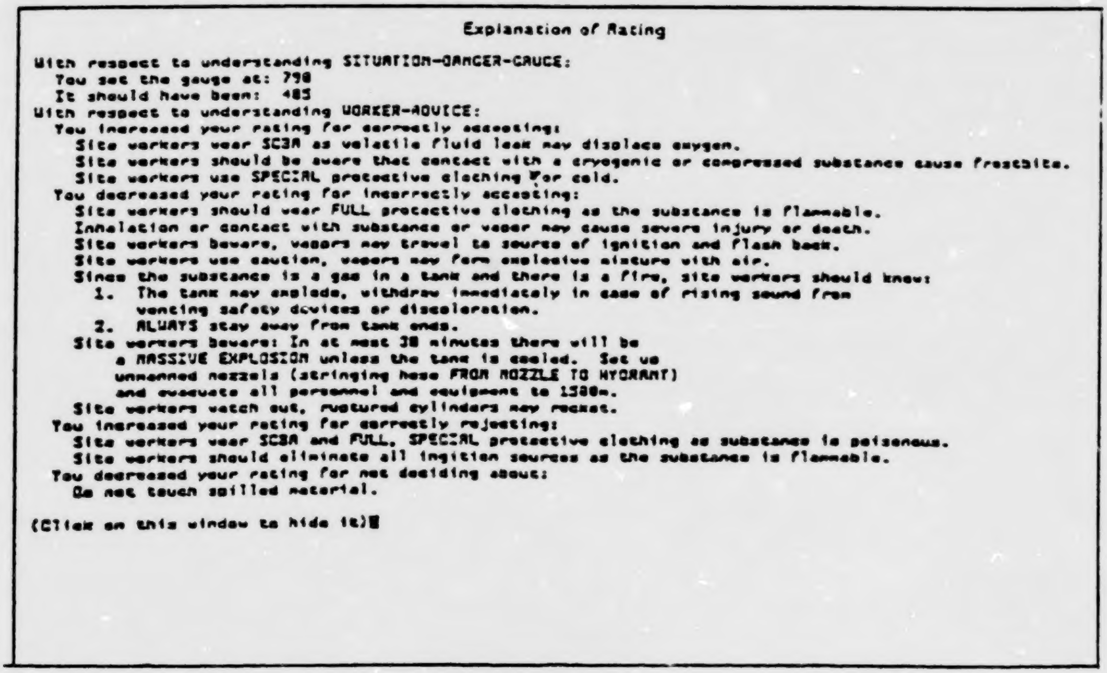
In brief, the HERMES interface allows the user to participate in every activity presented on the screen, and in any order. This flexibility relates to the expert's own emergency response process of making decisions as the information arrives. This has the advantage that the user is not forced into a fixed sequence of questions and answers.

The HERMES Tutorial System

The tutorial system makes use of the same set of emergency response knowledge as that in the expert advising mode. This implies that the student is able to conveniently access public knowledge usually available in reference materials, and private knowledge usually available in consultation with an expert.

In tutorial mode (Figure 3), the student is given a choice of lessons. Each lesson presents a different scenario to the student, automatically setting up the SCENE canvas, weather conditions and the variables in the INCIDENT MENU. To gain experience in the area of hazard assessment, the student is allowed to set the readings on the evacuation distance gauge, the situation danger gauge, the explosion danger gauge or the fire danger gauge in the SET THESE LEVELS window. Taking and rejecting site advice, public advice, worker advice or environment advice are additional teaching goals. A set of advice of the different types are given in the PICK ADVICE FROM THIS LIST window. The student then distributes these into either the ADVICE YOU PICKED window or the ADVICE YOU REJECTED window.

The student can obtain feedback on his performance by clicking the mouse on the "rate me" button in the TUTORIAL CONTROL window. This will cause the gauge labeled "Your Rating" to



```
                                   Explanation of Rating

With respect to understanding SITUATION-DANGER-GAUGE:
  You set the gauge at: 790
  It should have been:  485
With respect to understanding WORKER-ADVICE:
  You increased your rating for correctly accepting:
    Site workers wear SCBA as volatile fluid leak may displace oxygen.
    Site workers should be aware that contact with a cryogenic or compressed substance cause frostbite.
    Site workers use SPECIAL protective clothing for cold.
  You decreased your rating for incorrectly accepting:
    Site workers should wear FULL protective clothing as the substance is flammable.
    Inhalation or contact with substance or vapor may cause severe injury or death.
    Site workers beware, vapors may travel to source of ignition and flash back.
    Site workers use caution, vapors may form explosive mixture with air.
    Since the substance is a gas in a tank and there is a fire, site workers should know:
      1.  The tank may explode, withdraw immediately in case of rising sound from
          venting safety devices or discoloration.
      2.  ALWAYS stay away from tank ends.
    Site workers beware: In at most 30 minutes there will be
        a MASSIVE EXPLOSION unless the tank is cooled.  Set up
        unmanned nozzels (stringing hose FROM NOZZLE TO HYDRANT)
        and evacuate all personnel and equipment to 1500m.
    Site workers watch out, ruptured cylinders may rocket.
  You increased your rating for correctly rejecting:
    Site workers wear SCBA and FULL, SPECIAL protective clothing as substance is poisonous.
    Site workers should eliminate all ingition sources as the substance is flammable.
  You decreased your rating for not deciding about:
    Do not touch spilled material.

(Click on this window to hide it)█
```

Figure 4. The Explanation Facility in the Tutorial System

give some indication of how well the student has performed in the current lesson. For setting a gauge, the student receives a rating based on how closely he approximates the reading the expert system generates for the gauge. When picking and rejecting advice, the pupil increases his rating by making correct decisions and decreases it by making incorrect ones. Also, the rating is lowered for not deciding about some pieces of advice (leaving them in the PICK ADVICE FROM THIS LIST window), but the deductions are not as harsh as for making the wrong decision. The rating is currently divided evenly between each purpose and, of course, perfect and zero ratings result for doing everything right and wrong respectively.

To learn more about his rating, the student can click on the "explain" button in the TUTORIAL CONTROL window. This will give him a complete explanation of his performance on the current lesson (Figure 4). For gauges, the pupil can read the value he set the gauge at and the value it should have been set at. For advice groups, a complete breakdown of what was done and what should have been done is given for each piece of advice.

DEVELOPMENT DETAILS

The first task in developing HERMES was to determine the knowledge involved in emergency response management. General concepts were taken from the reference manuals and were quite straightforward. Eliciting knowledge from the human expert was a more involved process. Knowledge acquisition is usually considered the bottleneck in developing expert systems [1] and this project was no exception. While the expert was cooperative and enthusiastic, the knowledge he brought to bear on each problem was difficult to articulate. The rules were acquired by discussing different situations and appropriate responses for each. Then the significant details for each situation were deduced by asking how the advice would change as specific input variables change. For instance, the evacuation distance was determined to be 1500 metres for a leaking flammable gas such as propane. However, it was discovered that a non-flammable non-poisonous gas such as nitrogen required an evacuation distance of only 800 metres. At this point, having established that substance properties have a direct effect on evacuation distance, it was an easy task to proceed through many substances and acquire the heuristics for setting the evacuation distance.

The problem was then implemented using the expert system tool ART (Automated Reasoning Tool) by Inference Corporation running on a Symbolics 3620 LISP machine. ART offers high level routines for using schemata, relations, inheritance, forward chaining, backward chaining, graphics and menus, to name a few. Since this project was a feasibility study, it was of great help to spend minimal time developing primitive knowledge representation, inference, and

Scenario 1.	Anhydrous ammonia pup over turn, leak of 100 l/min, wind 9 km/h from SW, farm house 200 m to NE.
Scenario 2.	Nitrogen tanker collision, gouges in tank, truck on fire, could spread to impinge on tank.
Scenario 3.	Propane cylinder carrier roll over, several damaged cylinders, smell of propane in air.

Figure 5. Case Studies for Evaluation

interface routines. This choice allowed focusing most of the limited project time (4 months) on demonstrating that the problem is solvable.

Some time was then spent on the evaluation of the performance of HERMES. A second expert not involved in the study was asked to compare the advice given by HERMES on three case studies (Figure 5) with what he would have suggested. Furthermore, the expert was asked to provide feedback on the user interface and ease of use of the entire system. The results proved very satisfying. However, there were instances of differences in opinion due to flaws in the rule base which were easy to fix. Concerning the user interface, the objective expert was pleased with the system's environmental modeling for generating the concentration area. As well, he enjoyed learning and using the system. However, he did bring a very good point with respect to the input interface: the explicit specification of the quantity of the substance involved should be included. Many important inferences could be made from this piece of data including, for instance, when all of the substance will have escaped. The expert also noted that the system was, in some circumstances, a little sluggish. This problem is mainly due to the numeric calculations related to the concentration area. This problem can easily be rectified as the current algorithm was selected based only on how easy it was to encode; so there is much room for optimization.

CONCLUSIONS AND FUTURE DIRECTIONS

The goal of the HERMES project was to investigate the feasibility of constructing an intelligent assistant and tutor in the domain of emergency response management. A prototype expert system was implemented and evaluated by an objective third party. As a feasibility study, the project is strongly successful. To extend the prototype towards a usable product however, several issues must be considered concerning the expert system, the tutorial system, and the implementation issues.

Future Work

Knowledge Base For a more useful system, it is desirable that the system is able to deal with all possible substances and situations. A ready approach is to extend the knowledge base with rules for representing the additional substances and situations. However, this would predictably result in an inefficient system, as is the case in many enumeration driven systems. An alternative approach would be to represent substances by their physical and chemical characteristics. Substances can then be grouped into classes and inferences may be made to refer to the properties in the class of a substance and not to the specific substance being considered. The knowledge base must then be modified to implement a classification hierarchy.

Dealing With Uncertainty One area where little work has been done is in giving the system the ability to deal with uncertain facts and to then propagate this uncertainty through to conclusions. The present system incorporates rudimentary uncertainty in specific areas but a general scheme would be much more useful. If the user were allowed to input the reliability of the input values, the system could use this information to indicate how much confidence can be placed in any piece of advice it gives.

Environment Modeling There are many other models of the environment that could be used in the system. The present system only models how a substance may move through the air, but there exist well defined models for absorption of substances in soil, and how they behave in water. Also, leak flow rates can be determined solely from an estimate of the size of the hole in the containing vessel. Another important point on the topic of environment modeling is that there are often several models for a system, each valid under a certain set of assumptions. This fact opens up the possibility of building an expert system to choose the most appropriate model for the situation.

Data Base Interface A problem related to environment modeling that would have to be solved is that many of these mathematical models require very specific and precise chemical information as input. Fortunately, large commercially available data bases exist to supply this data. Therefore, it would probably be useful to interface HERMES with one of these data bases. Another application for data base interface becomes apparent in the difficult situation where an accident happens in an urban area. In this case, it is certainly not practical for the user to enter all the relevant details of the scene. However, in many cases, there will be this kind of detailed information available in databases. The ability for the system to access these city plans, terrain maps, and soil type maps, along with the ability to scale the scene, would undoubtedly be an invaluable addition to the system.

Temporal Reasoning When one analyzes a hazardous substance incident, he realizes that it is in fact a sequence of events. Consequently, the system could gain a great deal of power if it had some sense of time. An example of how time dependency could be used is in the environmental models. Presently, when the concentration area is calculated, it is assumed that the chemical leak will continue for an extended period of time. If the system depended on a clock, the concentration could move across the scene in real time and react appropriately once the user indicates that the leak is slowed or patched. Similar considerations apply to any other environmental models the system may use. Another application of this temporal model is in the area of emergency planning. At any given time, there are only finitely many resources available for duties such as, for instance, fire fighting. Using a temporal reasoning system, the system could deduce the most effective way to schedule the available resources and make suggestions about what additional equipment would be valuable. Evacuation planning is also another excellent application for this procedure.

Report Generation With the addition of time dependent reasoning, it would be possible for the system to automatically generate reports for the incidents it handles. Once a substantial number of these reports exist, the system could critique them in retrospect. In this way, it is conceivable that the system could suggest innovative modifications to the rule base. Of course, experts would still have to carefully evaluate the proposed changes.

Explanation Facility Most well designed expert systems have an explanation facility. Though little work has been done in HERMES to implement this feature, it would be relatively easy to implement a complete explanation system. However, this is practicable only if the system has a deep model of its problem domain and this task is too complex for this prototype application.

Tutoring System As with the expert advising mode, there are several opportunities for extensions and additions in the tutoring system. One interesting extension should be to allow the student to place evacuation and concentration areas on the scene. Then, the system can execute some kind of matching between the area the student defined and its corresponding area, generating a measure of the quality of the match. Another unimplemented capability that the tutorial system should have is the ability to monitor the student's performance. If this system existed, the student would be led through a series of incidents and he would automatically be given remedial situations if his performance should slip. In this way, it would be possible for the system to certify pupils as having mastered certain concepts upon completion of a system defined course. Finally, a skill that the disaster expert must possess is the ability to ask the right questions in the often brief and sparse phone contact he has with the accident scene. This skill could be taught by the tutorial system through a simulation of the phoning process. Each time the student is in contact with on-site personnel, he will be allowed to ask any number of questions. Some of these questions may be answered right away, others will be answered in the next phone contact. Using this simulation, the student must learn to ask the right question, or he will be penalized for not being able to give important advice due to lack of information.

Implementation Concerns When considering what kind of computer software and hardware to build a complete version of HERMES on, many factors are involved. First, it must be decided what functionality is needed of the expert system tool. Frames, inheritance, forward and backward chaining rules, procedural attachments, and certainty factors are standard features in most high-end tools such as ART on the Symbolics by Inference Corp. and GoldWorks by Gold Hill Computers on the IBM PC/AT, and as such are suitable tools for development. For the other factors involved in implementation decisions such as development cost, delivery cost, speed, software portability, and user interface considerations, tradeoffs will have to be weighed. For instance, using GoldWorks will minimize costs but will not provide a powerful interface as with ART.

Final Remarks

While working on this project, it became apparent that expert system technology can be very useful when applied to the problem of emergency response management. It can be utilized on a large scale, for example, a government agency or municipality; or the technology can be used on a smaller scale as in a single industrial site. It is clear that HERMES is not only a useful aid to the duty manager, but also serves to extend his abilities in several ways. For instance, the emergency response team seldom has time to work out poisonous gas concentrations, but HERMES can do it near instantly. Also, HERMES never overlooks subtle variables that the duty manager may miss in a stressful situation where a decision is needed immediately. The complete version of HERMES may be extended to do complex temporal planning that is too data intensive for humans to perform. Ultimately, it may be possible for HERMES to suggest previously unknown useful emergency response techniques.

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CLEAN-UP OF PCB-CONTAMINATED WASHWATER BY REVERSE OSMOSIS AND ULTRAFILTRATION

Jill Worry, Diane Radnoff & Harry Whittaker

1.0 Introduction

In November 1987, Environment Canada was approached concerning the treatment of 2000 litres of PCB-contaminated washwater generated from a previous clean-up. The washwater was contained in barrels which ranged in concentration from 10 ppm to 641 ppm PCB.

Harry Whittaker of the Environmental Emergencies Technology Division (EETD) of Environment Canada recommended the use of a lab-scale reverse osmosis (RO) unit with Filmtec (UFP 4040) spiral wound membranes to reduce the volume of the contaminated water to approximately 200 litres and to produce a permeate suitable for discharge at less than 3 ppb PCB. A similar clean-up had been conducted successfully by Mr. Whittaker and Environment Canada personnel in March 1984 and the results were presented at the Second Annual Technical Seminar on Chemical Spills held in Toronto, Ontario on February 5, 1985.

It was predicted that the treatment, which commenced on November 25, 1987 at federal government facilities in the National Capital Region, would take eight days. Initial laboratory filtration tests indicated that the feed would have to be pre-treated with a filtration system to remove the high concentration of particulate (mostly coal fines) and the black oil which formed a thin layer on the surface. The failure of this system made treatment of the water with RO infeasible. Since rapid, irreversible fouling of the membranes would have resulted from treating the feed in this condition, it was necessary to find another solution and the treatment was delayed.

As a result of the previous success of ultrafiltration (UF) in the treatment of oily solutions with a high concentration of suspended solids, two tubular polysulphone UF membranes (BSC blend,hydrophilic) were purchased from Zenon Environmental Inc. Although the quality of the ultrafiltrate was found to be excellent, (the level of PCBs was less than 3 ppb), the flowrate was below acceptable limits. The treatment would have taken forty days and sufficient ultrafiltrate could not be generated in a reasonable time to clean the membranes properly.

A recirculation heating system was installed in the feed tank as the flowrates were temperature dependant and the surrounding outdoor temperatures had fallen to below 0°C. As well the feed was acidified with hydrochloric acid (HCl) to pH 5 to prevent calcium carbonate build-up on the membranes and to remove any scale that may have already formed. The acidification and heating changed the nature of the feed. Its colour changed from grey to brown and the coal particulate appeared to settle out at the bottom of the tank much more quickly. Vapours with a distinct odour evaporated off the surface of the tank. The high flowrate of the recirculation heating system and the presence of a membrane detergent in the holding tank caused the coal fines to froth. The froth was then skimmed off the surface of the tank with a sieve containing Matasorb(R)M100 particulate. Although the ultrafiltrate flowrates increased slightly, further filtration tests showed that filtration/RO could now be utilized as well.

When there was approximately 400 litres of concentrated feed left to treat, two granular activated carbon (GAC, 20x50 mesh) columns were set up in parallel to the filtration/RO and UF systems. The quality of the GAC effluent was unacceptable for discharge (36 ppm PCB). Therefore, the columns were used as a granular filter for the feed, that is as a pre-treatment to filtration/RO or UF, to prevent any further fouling of the membranes.

Since many of the barrels contained sludge, the total volume treated was approximately 1200 litres. The volume of contaminated washwater was reduced to 25 litres (essentially the system hold-up volume) and 26 kg of GAC (solid waste) were generated. Four barrels were cleaned to less than 5ppm PCB.

The treatment required 21 days and cost approximately $7250 including operator costs, shipping, expendables (power, disposable parts such as filters etc.) and equipment rental costs.

2.0 Background

The source of the PCB-contamination was originally a commercial heat transfer fluid known as Therminol FR-1 manufactured by the Monsanto Corporation. This fluid contains 100% Aroclor(R) 1242. Sources of information on the chemical properties and toxicity of this fluid are given in the references.

Therminol FR-1 was removed from use in 1980 and replaced with a non-PCB-containing fluid called Therminol-66. When the Therminol-66 was subsequently removed and collected (six months later) the level of PCBs in the barrels ranged from 36,300 to 45,500 ppm. The replacement fluid, Therminol-55, normally a non-PCB-containing fluid, currently has a level of PCBs of less than 10 ppm. However, some samples taken in 1987 in sewers and gutters downstream of the equipment containing the Therminol-55 were found to have a concentration that exceeded 50 ppm PCB. The PCB contamination, whether caused by an equipment leak or a spill when the Therminol-66 was replaced, necessitated a clean-up of the contaminated gutters and sewers. This was conducted, generating the washwater, the storage of which presented the problem. The waste could not be incinerated (as waste oil) because of its high concentration of PCBs.

3.0 The Treatment

3.1 The Filtration System
(cf. Figure 1)

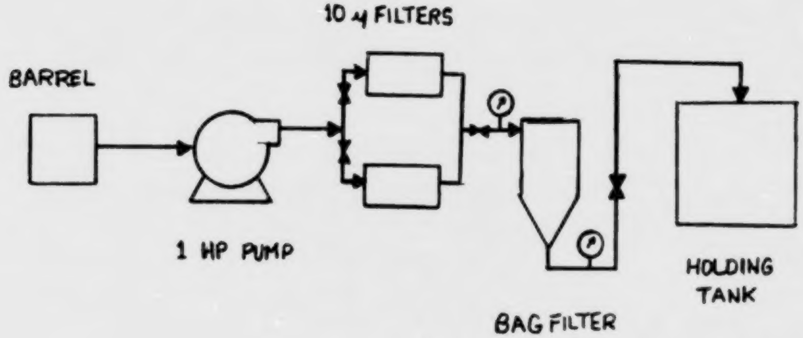


Figure 1: Schematic of the Filtration System

The filtration system was a requisite pretreatment to RO but also a treatment method in itself. Since PCBs are not very soluble in water, (H_2O_{25} sol. of Aroclor$^{(R)}$1242 - 240 x 10^{-6} g/L), the PCBs were likely adsorbed on the particulate or dissolved in the oil. The filtration system would therefore remove a significant quantity of the PCBs with the removal of the oil and particulate.

The first step in this treatment was the transfer of the liquid from the barrels into a holding tank via the filtration system. A 1 Hp centrifugal pump was required to transport first the highest concentration liquid (641 ppm PCB) and then the lowest concentration liquid (10 ppm PCB) through a 10 micron cartridge filter and then through a 1-3 micron woven polypropylene bag filter manufactured by Ronningen-Petter. The pressure drop of 207 kPa (30 psi) was 20 times greater than the pressure drop of 10 kPa (1.5 psi) expected at the maximum flowrate. More significantly, the quality of the filtrate was no better than the quality of the feed.

A backpressure valve was inserted to control the pressure drop across the bag filter but this did not improve the quality of the filtrate and decreased the filtrate flowrate.The bag filter was partially filled with Matasorb$^{(R)}$M100 particulate but the filtrate quality was not enhanced and the bag filter plugged immediately. A gravity filtration test showed that the bag filter itself was passing the coal particulate. A de-emulsifier was added to the feed (5 mL/100 L of feed) but this also had no effect on the quality of the filtrate. No other manufacturers were found that produced a bag filter which was compatible with the filter housing and therefore, it was necessary to find another solution.

Several other filter media were then tested using gravity filtration. A sand and gravel (1mm-1cm dia. particles) filter was examined but the filtrate quality was poor. An Oclansorb$^{(R)}$ (a chemically treated peat moss with oil sorbing qualities) filter gave the same result. The quality of the filtrates from a GAC filter bed and a 5 micron cartridge filter (string wound, made by Hytrex) were comparatively better especially when the feed samples were shaken before pouring, but they still contained too much particulate for RO treatment. The filtrate flowrates were unacceptably slow in all four media. Ultrafiltration seemed to be the best option at this point because no pre-treatment of the feed was necessary and ultrafiltrate flowrates of at least 1 Lpm were expected.

3.2 Ultrafiltration

(cf. Figure 3)

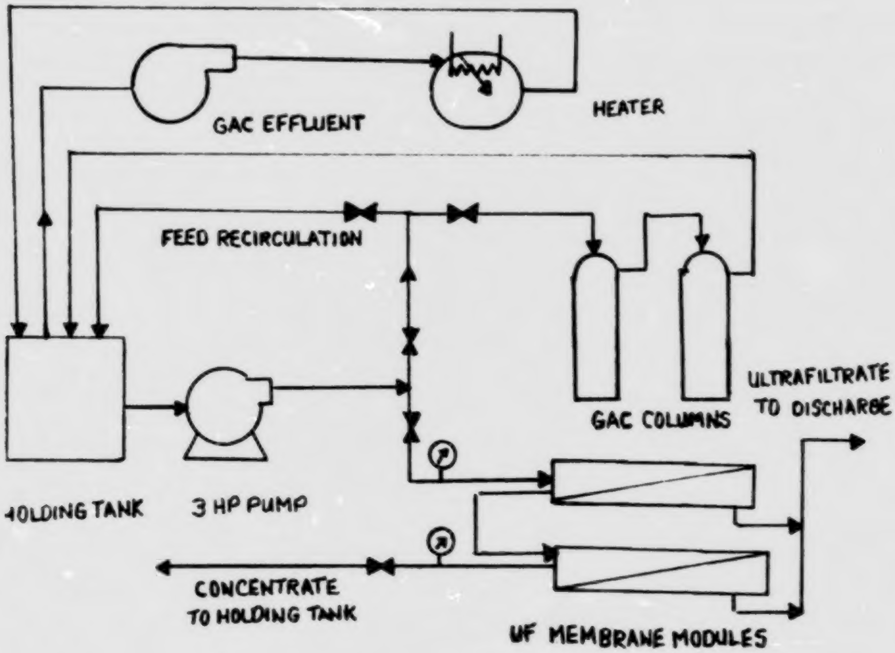
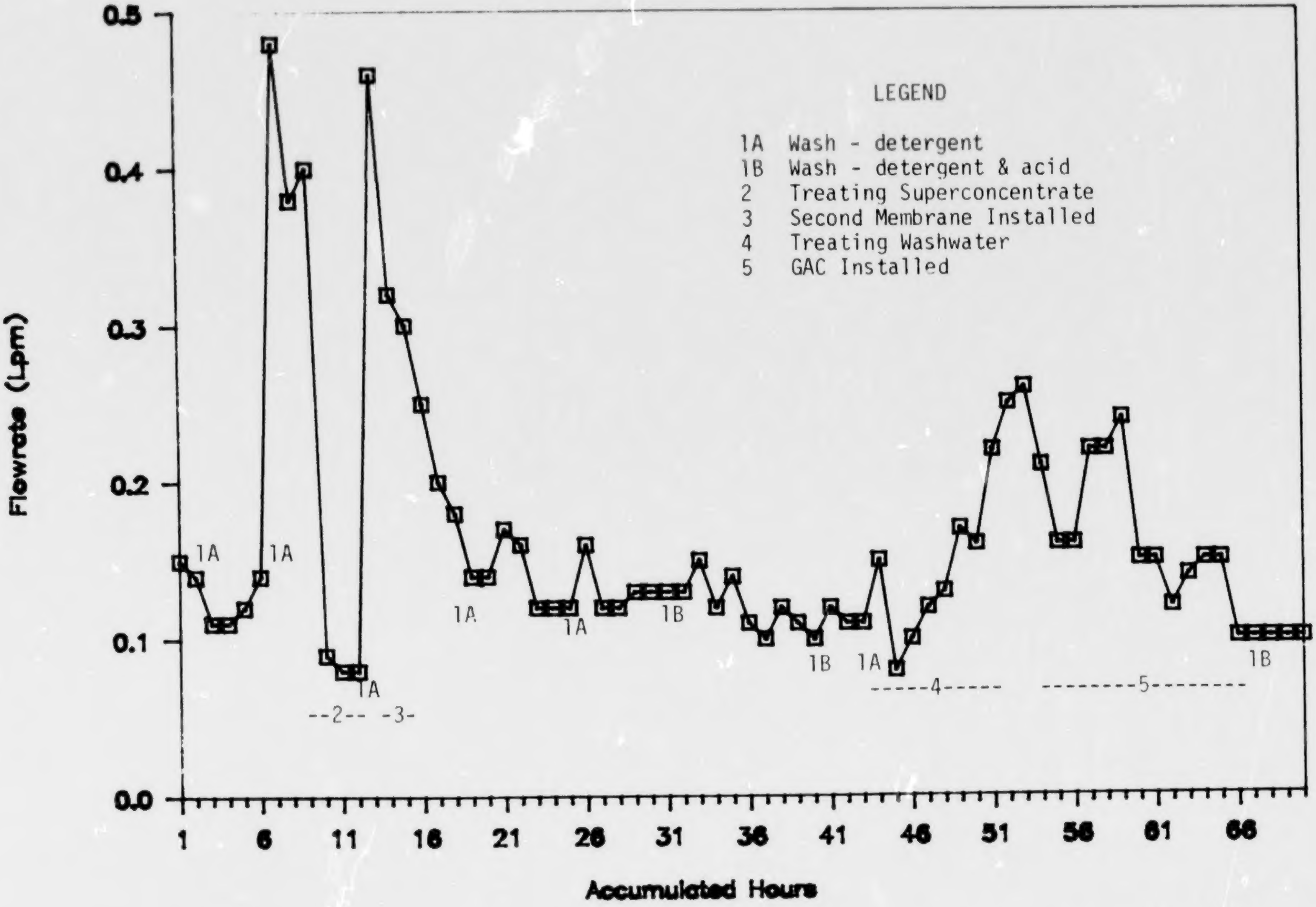

GAC EFFLUENT
HEATER
FEED RECIRCULATION
GAC COLUMNS
ULTRAFILTRATE TO DISCHARGE
HOLDING TANK
3 HP PUMP
CONCENTRATE TO HOLDING TANK
UF MEMBRANE MODULES

Figure 3: Schematic of Ultrafiltration System

The UF system required turbulent flow across the membrane; a feed flowrate of 136 Lpm (30 Igpm), an inlet pressure of 415 kPa (60 psig) and a pressure drop of 207 kPa (30 psi). To achieve this, a 3/4 Hp centrifugal pump was placed in series with the 1 Hp pump. This gave an inlet pressure of 346 kPa (50 psig). In terms of quality, the ultrafiltrate was suitable for discharge. However, the flowrate was only 0.1 Lpm. The module was cleaned and flow-tested with tap water and gave an ultrafiltrate flowrate of only 0.45 Lpm.

Figure 2: UF Ultrafiltrate Flowrates



Following consultation with Zenon Environmental Inc., a 3 Hp pump and another UF membrane module to be used in series with the first were brought into service. With water, the ultrafiltrate flowrate of the two modules was 0.75 Lpm. The initial flowrate of the two modules in series when treating contaminated feed was 0.48 Lpm at an inlet pressure of 173 kPa (25 psig) which was the best pressure that could be achieved.

The flowrates dropped steadily over the next two days to 0.10 Lpm despite the fact that the membranes were cleaned at the end of each day (cf. Figure 2). It was decided to heat and acidify the feed at this point. A 3000 W recirculation heater was utilized rather than an immersion heater because it would promote good mixing in the holding tank. The change in the nature of the feed due to the frothing and the subsequent removal of the coal particulate and fines then made it feasible to use filtration/RO. The baseline water rate of permeate determined at the beginning of the trial was 3 Lpm and it was estimated that the permeate flowrate with the feed would be at least 1.5 Lpm.

The UF system was then operated in parallel with filtration/RO. It was used to treat the spent cleaning solution which was more dilute than the feed. The ultrafiltrate flowrate was recovered to 0.25 Lpm. When the UF system was returned to the feed, the ultrafiltrate flowrates dropped again and remained between 0.10 and 0.15 Lpm even when the GAC columns were used as a granular filter for the feed.

3.3 Reverse Osmosis
(cf. Figure 5)

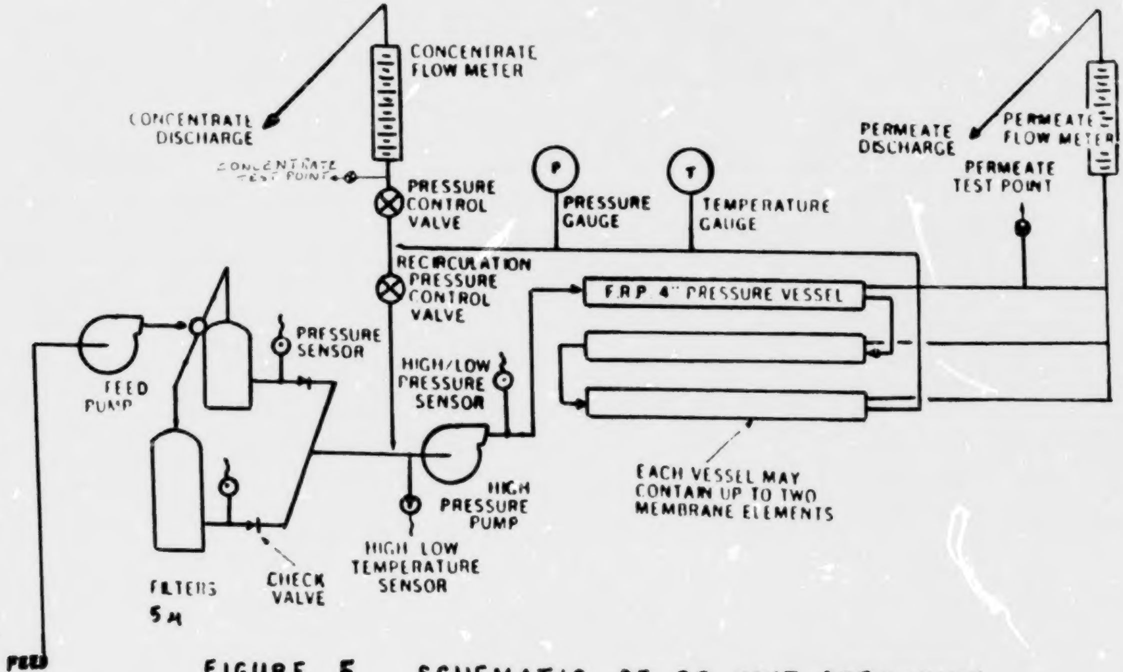
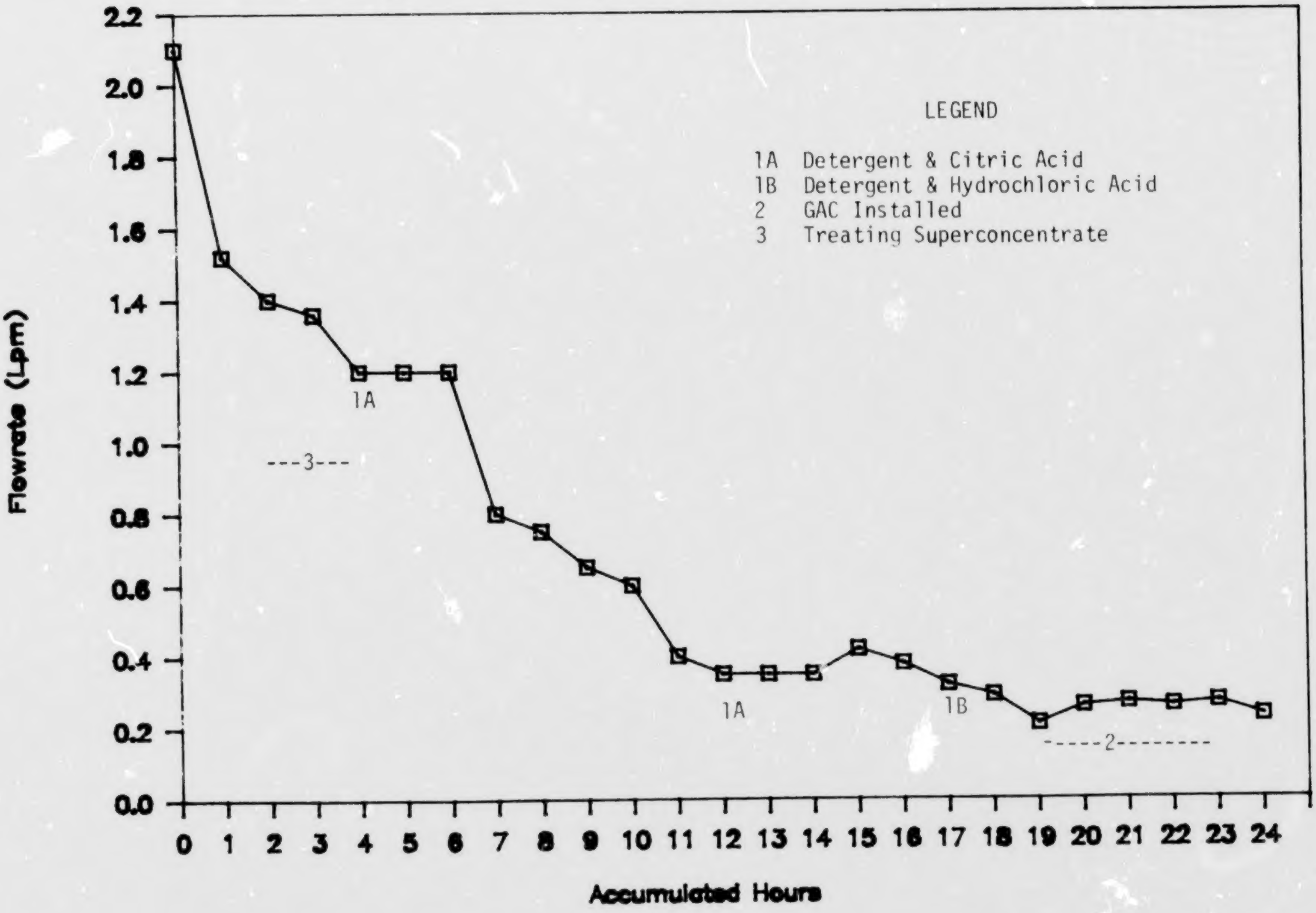

CONCENTRATE FLOW METER
CONCENTRATE DISCHARGE
CONCENTRATE TEST POINT
PRESSURE CONTROL VALVE
P
PRESSURE GAUGE
T
TEMPERATURE GAUGE
PERMEATE DISCHARGE
PERMEATE FLOW METER
PERMEATE TEST POINT
RECIRCULATION PRESSURE CONTROL VALVE
F.R.P. 4" PRESSURE VESSEL
PRESSURE SENSOR
FEED PUMP
HIGH/LOW PRESSURE SENSOR
HIGH PRESSURE PUMP
EACH VESSEL MAY CONTAIN UP TO TWO MEMBRANE ELEMENTS
HIGH LOW TEMPERATURE SENSOR
FILTERS 5 μ
CHECK VALVE
FEED

FIGURE 5 SCHEMATIC OF RO UNIT OPERATION

Figure 4: RO Permeate Flowrates



The RO lab-scale unit was operated between 5184 and 5530 kPa (750-800 psig) pressure and at a temperature between 18.5 and 36.3°C (65-97°F). The feed was filtered through two 25 micron cartridge filters (string wound, made by Hytrex) before entering the unit. It was only necessary to change these filters once during the 24 hours the unit was in operation.

Initially the permeate flowrate was higher than the concentrate flowrate at a ratio of 2.7:1. The permeate flowrate of 2.1 Lpm was 1.5 times higher than expected. Although a lower concentrate flowrate could be achieved (.5 Lpm), it was adjusted to .75 Lpm at 5184 kPa (750 psig) to prevent fouling of the membranes. The permeate flowrates decreased and the concentrate flowrates increased to a ratio of 1:1 after two hours of operation (cf. Figure 4).

The cleaning procedures did not recover the permeate flowrates or help to maintain them. This indicated that the membranes were irreversibly fouling as the feed became more concentrated. Two GAC columns were therefore set up in series and operated at an effluent rate of 0.6 Lpm to both adsorb the contaminants and act as a feed filter. The permeate flowrates subsequently increased slightly from 0.21 to 0.27 Lpm unlike the UF flowrates which remained constant between 0.10 and 0.15 Lpm.

With only 400 litres of feed left to treat, a gasket on the high pressure pump failed. It was decided to finish the treatment with GAC and UF as this would require less time than it would to procure another gasket and fix the pump.

3.4 Lab Analysis

The lab analysis was performed by Bondar-Clegg & Company Ltd. of Gloucester, Ontario. The method used was gas chromatography with a packed column and an electron capture detector. This method is used to screen for the presence of PCBs (specifically Aroclor(R) 1242,1254 and 1260) in transformer oil and therefore it was necessary to modify the procedure for aqueous solutions by extracting the PCBs in the sample into hexane. The complete procedure and the equipment used is discussed in the article given in the references.

The major advantages of this method are that sample preparation is simple and analysis is quick. Sixty-seventy assays can be run per day.

3.5 The Containment System

To protect the surrounding environment from any spills or equipment leaks, a containment system was built and the equipment was then installed on top of it. This consisted of a frame (like a shallow trench) with a pressboard bottom and plywood (1 by 4's) sides upon which sheets of polyethylene and Matasorb(R)M95 respectively were spread and stapled.

The containment system was very effective. The wood from the frame construction was salvaged when the treatment was completed as it was re-usable.

3.6 Cleaning Procedure

The UF membranes were first cleaned with an alkaline detergent solution (pH 11) which was recirculated through the system at the operating pressure. Acid solution (HCl, pH 1) was then flushed through the system at a lower pressure achieved by leaving the recirculation valve open. Although the detergent appeared to remove a large quantity of oil and particulate (ie. the cleaning solution became very dirty very quickly) the flowrates did not improve significantly.

The RO Filmtec membranes had been previously used in a pesticide residue treatment in Saskatchewan in the Fall of 1987. Therefore at the beginning of this treatment they were cleaned with detergent and acid and then flushed with tap water to determine the baseline permeate rate. Sodium metabisulphate was added to the tap water to remove free chlorine which can oxidize the membranes. As well as detergent washes, both HCl washes (pH 2) and citric acid washes (pH 3) were performed. The full cleaning procedure of flushing the system with permeate, recirculating the cleaning solution at low pressure (1382 kPa) and then flushing with permeate again required at least 200 litres of permeate.

Since this quantity of permeate/ultrafiltrate could not be generated before the flowrates began to fall and the cleaning procedures did not improve the flowrates, an end-of-day cleaning procedure was adopted which minimized the amount of permeate/ultrafiltrate used. (If the cleaning procedures had improved the flowrates, tap water could have been used for cleaning. In this case large quantities of water would have become contaminated and then would have had to be treated.) The procedure was:
1)The system was flushed and the water was then returned to the wash barrel.
2)Detergent was added to the flush water and this was recirculated through the system for twenty minutes. This solution was heated with the recirculation heating system and left in the membranes over night.
3)In the morning, acid was added to the detergent solution and recirculated for ten minutes. The wash solution was then pumped to the feed tank.
4) The system was then flushed with 100 litres of permeate which was then returned to the wash barrel for the next wash.

Four barrels were cleaned to meet the requirement of a level of PCBs of less than 5 ppm w/w. A sample was taken from the barrel that had contained the highest concentration (641 ppm) of PCBs. The level of PCB in 4 litres was found to be 6 ppb. The cleaning procedure was:

1)Sludge in the barrel was manually transferred with a coal shovel to a pail and ultimately to another barrel and the sides and bottom of the barrel were dried with Matasorb$^{(R)}$.

2)The barrel was scrubbed with a concentrated membrane detergent solution (100 g/L) using a vegetable brush. The sides and bottom were wiped dry with Matasorb$^{(R)}$.

3)The barrel was rinsed with 0.5 litres of acid (HCl) solution and then rinsed with 2.5 litres of tap water. The solution was removed and the barrel was dried as before.

4.0 Results/Discussion

4.1 The Filtration System

One possible explanation for the failure of the bag filter in this treatment is that the feed was bypassing the bag filter. In this bag filter unit, a flat gasket between the bag filter and the strainer basket created the seal which should have prevented the feed from entering the filter housing. Larger units contain in addition to a gasket, an envelope seal. It is possible that an envelope seal might have prevented this failure if this was the problem. The problem may also have been that the feed was bypassing the filter at the point where the bag fabric is stitched on to the lip of the bag. It was difficult to ascertain which one of these problems, if either, was responsible for this failure as the bag filter is a closed system A gravity filtration test seemed to indicate that the bag itself was incapable of filtering the waste. An emulsion that was not broken by the de-emulsifier may have caused this. Materials other than polypropylene such as bonded nylon, polyester or teflon could have been investigated for suitability with this feed. Dry Con Ltd., the supplier of Ronningen-Petter products in the Ottawa area, is still investigating the cause of this failure and the results are not yet available.

4.2 Ultrafiltration

The baseline ultrafiltrate flowrates were 50% lower than expected. Based on a baseline fluxrate for these membranes of 2 m^3/m^2/day and a surface area of .68 m^2/membrane, an ultrafiltrate flow of 0.95 Lpm for one module was expected and a flowrate of 0.45 Lpm was achieved. One possible reason for this was that the flow across the membrane was insufficient. The flow into the membrane was not measured with a flowmeter because the feed was so dirty that it would have been impossible to read. The concentrate flowrate out of the membrane was fast and therefore difficult to measure with any degree of accuracy. (One measurement ranged from 41 Lpm to 91 Lpm.) The pressure gauges were not reliable. They had a tendency to become obstructed by the viscous and oily feed. There was no correlation between the pressure readings and either the permeate or concentrate flowrates. However, even disregarding this fact, the desired inlet pressure was never achieved. The desired inlet pressure was 417 kPa but the highest inlet pressure achieved was 346 kPa.

Another possible explanation for the low ultrafiltrate flowrate was the presence, in either the tap water or the feed, of a cationic surfactant which can do irreversible damage to the membrane. This phenomenon was indicated by the sharp drop in membrane performance shortly after start-up. Although an initial drop was expected due to compaction of the membrane the magnitude of this drop was much greater than expected and the membranes did not recover with cleaning. A 10,000 MW size particle or colloid could also plug the pores of the membrane irreversibly. A module was returned to Zenon Environmental Inc. following the treatment to determine if it could be regenerated but the results of this analysis are not yet available.

4.3 Reverse Osmosis

The Filmtec membrane is usually a single use membrane when it is used for spill clean-ups. When treating organic chemicals in water they tend to become irreversibly fouled and usually can not be regenerated. With inorganic chemicals the membranes have better recovery and regeneration rates. Prior to this PCB treatment, the Filmtec membranes used had treated 12,000 litres of pesticide-contaminated wastewater with a high concentration of particulate. At start-up four Filmtec membranes in series delivered a permeate flowrate of 10 Lpm but this rate fell over the course of the pesticide residue treatment to 2 Lpm and did not recover.

In light of this, the permeate rates of the RO system were actually higher than expected. With a baseline water rate of 3 Lpm for two Filmtec membranes in series, a flowrate of 1.5 Lpm was expected and a flowrate of 2.1 Lpm was achieved initially. The trend shown in the graph of the flowrates versus time is typical of the Filmtec membrane except that it is usually possible to recover the permeate flowrate with cleaning.

A composite sample of permeate from three of the barrels met the requirement of a concentration of less than 3 ppb PCB. One sample however, taken directly from the lines when the RO system was treating superconcentrate (2nd pass concentrate), contained a level of PCBs of 10 ppb. This sample was not believed to be a representative sample of the bulk permeate quality but it indicates that the exclusion of the membrane (20,000 M.W. cut-off) was just adequate for this treatment.

5.0 Conclusions

It was not determined analytically how far the UF membranes exceeded the requirement of a level of PCBs of less than 3 ppb since it is beyond the capability of the lab equipment and method used to do so with any degree of accuracy. It might be possible then that a lower exclusion UF membrane (a membrane with a M.W cut-off greater than 10,000) with a higher fluxrate could be utilized to meet the given requirement.

The cost of this treatment was not typical because suitable RO membranes were available. If it had been necessary to purchase new membranes the treatment cost would have been higher. On the other hand, the operator costs (the major cost in this treatment) would have been lower because the treatment would likely have been completed sooner.

Overall the treatment was a success. The volume of liquid was reduced to 1/48 of the original volume of 1200 litres which exceeded expectations and the permeate was suitable for discharge with a concentration of less than 3 ppb PCB. Both UF and RO were shown to be viable methods of treating PCB-contaminated water.

6.0 Acknowledgement

The authors wish to thank Robert J. E. Philp, M.A.Sc., P.Eng for his patience, cooperation and knowledgeable advice during the treatment.

7.0 References

Lab Analysis

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RISK ASSESSMENT IN RAIL TRANSPORTATION OF DANGEROUS GOODS

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And

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Montreal, Quebec, February 9-11, 1988

INTRODUCTION

Hazardous materials management in an industrial society is becoming increasingly important due to increased use of hazardous materials and the increased demand for disposing of hazardous waste products. Safe transportation of hazardous goods is an integral part of hazardous materials management, and achievement of higher safety levels requires systematic identification of the areas in the transportation system components which contribute most to risk and their subsequent modification to reduce risk for more effective management.

The formation of the Toronto Area Dangerous Goods Rail Task Force was prompted by concern over public safety. The Task Force was given a mandate by the federal Minister of Transport to assess feasible means of reducing risk to the public from rail transport of dangerous goods through the Toronto area by:

1. Rerouting dangerous goods traffic on existing track using new rail operating plans.
2. Relocating dangerous goods traffic which would require new rail lines.
3. Other risk reduction measures such as technology improvements.

This paper summarizes work carried out for the Task Force. The work consisted of assessing the relative risks to the public of rail transportation of dangerous goods for various alternative routes and operational strategies and assessing the degree of risk reduction possible through such measures as technology improvements. Details of the work are given in CSC (1987). The risks assessed are those solely attributed to the dangerous goods that are transported.

Other risks associated with the movement of trains along rail lines also exist. These risks are those resulting from accidents such as train-automobile collisions at level crossings which do not lead to release of dangerous goods but can lead to fatalities of drivers or passengers of automobiles. Since the scope of this study focussed on dangerous goods only, these risks were not considered.

Background on Public Safety/Public Risk Considerations

For a concept so deeply routed in both technical and popular usage, "safety" has remained rather ill-defined. This vagueness has often resulted in the misuse of the term safety. We will therefore begin by defining this and some associated terms.

The first term we will deal with is "hazard", which is defined as any situation that has the potential for causing damage to life, property and/or the environment (e.g., a fire hazard due to a flammable liquid spill, toxicity hazard due to a toxic gas release, or explosion hazard due to the presence of explosive materials).

The next two terms we need to deal with are "safety" and "risk". The definition used in this study is that safety is a judgement of the acceptability of risk, and risk, in turn, is a measure of the probability and severity of harm to humans.

This definition contrasts sharply with the simplistic dictionary definitions that have "safe" as meaning something like "free from risk". Because nothing can be free from risk (one can't think of anything that isn't, under some circumstances, able to cause harm), nothing can be said to be absolutely safe. There are degrees of risk, and consequently there are degrees of safety. Notice that this definition emphasizes the relativity and judgemental nature of the concept of safety. Determining safety then involves two very different kinds of activities, as depicted in Figure 1:

1. risk analysis: measuring the probability and severity of harm - an empirical scientific activity, and
2. risk appraisal: judging the acceptability of risks - a matter of personal and social value judgement (a normative, political activity)

Note that these concepts and the methodology used in this study are similar to those in the draft CSA guidelines (CSA, 1987).

Scientists and engineers are prepared principally to assess only the probabilities and consequences of events, not their value to people. Thus, risk is the output of a scientific effort and it becomes the input to personal and social decision making. Now, risk is not an unfamiliar concept; it is involved at least implicitly in activities ranging from finance to romance.

Safety is obviously a highly relative attribute that can change from time to time and be judged differently in different contexts. This is primarily due to the fact that our knowledge of risks evolve, and so do our personal and social standards of acceptability.

Conducting a risk assessment involves estimating:

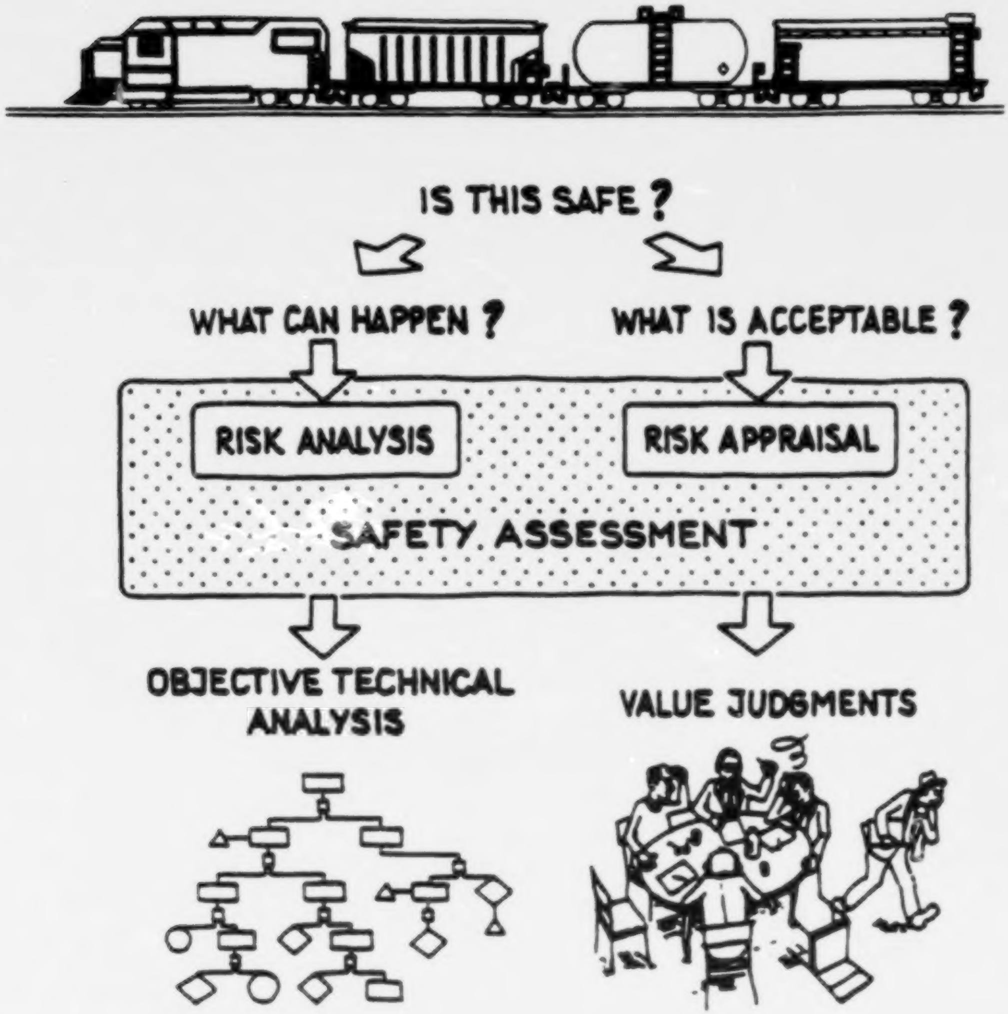
- probabilities (expected frequencies) of undesirable events
- consequences (severity of harm) to people of undesired events
- the associated risk in quantitative terms.

The undesired events in the context of this work are accidental releases of dangerous goods and these are described as "hazardous events" in this study.

We should now address the types and measures of public risk. The terms that are important here are "individual and societal risk" and "absolute and relative risk". Individual risk is defined as the risk of harm posed to an individual who is exposed to a particular hazardous activity. For example, the annual risk (or probability) of death due to smoking for an individual smoker is about 1 in 330. Societal risk, on the other hand, is defined as the risk that a number of people will be harmed from a societal group or the public at large who are exposed to a particular hazardous activity. For example, the risk or probability of death from smoking per 100,000 persons who smoke is about 300 deaths per year.

Absolute risk is defined as the probability of occurrence of specified consequences from all possible events associated with a particular hazardous activity; for example, the estimated number of fatalities per year from all possible hazardous release events associated with the transportation of

FIGURE 1


IS THIS SAFE ?
WHAT CAN HAPPEN ?
WHAT IS ACCEPTABLE ?
RISK ANALYSIS
RISK APPRAISAL
SAFETY ASSESSMENT
OBJECTIVE TECHNICAL ANALYSIS
VALUE JUDGMENTS

THE DIVISION OF THE SAFETY PROBLEM INTO THE TECHNICAL RISK ANALYSIS AND THE RISK APPRAISAL dangerous goods by rail in the Toronto area. On the other hand, relative (comparative) risks are the probabilities of specified consequences associated with the particular hazardous activity under alternative situations; for example, the risk from dangerous goods rail transport along two alternative routes. Taking the present Toronto rail system and operations as a baseline, then the risks associated with various alternatives can be examined relative to the existing or baseline risk. The purpose of the present risk assessment is to provide such estimates of the relative risks of dangerous goods transport in the Toronto area.

At this point it would be appropriate to deal with the question "Why assess risk?"

The process of risk assessment serves to organize thinking about risks, permitting technical judgements of interdisciplinary teams of experts to be integrated in a systematic manner.

The very process of performing a risk assessment

- leads to a better understanding of the risk inherent in a particular activity such as transport of DGs by rail;
- helps to identify risks that might not have been thought of otherwise;
- helps to identify steps that could be taken to reduce risks;
- motivates improvement in data collection by pointing out data base deficiencies.

Further, risk assessments can help to address two fundamental questions, one quantitative and objective and one qualitative and subjective:

1. What are the levels of risk?
2. What levels of risk are acceptable to the parties concerned?

The goals to minimize risks, to make responsible decisions and to take feasible courses of corrective action are the ultimate reasons for performing risk assessments. The results of risk assessments provide knowledge essential to informed decision-making.

STUDY AREA AND RAIL SYSTEM ALTERNATIVES INVESTIGATED

Geographic Location

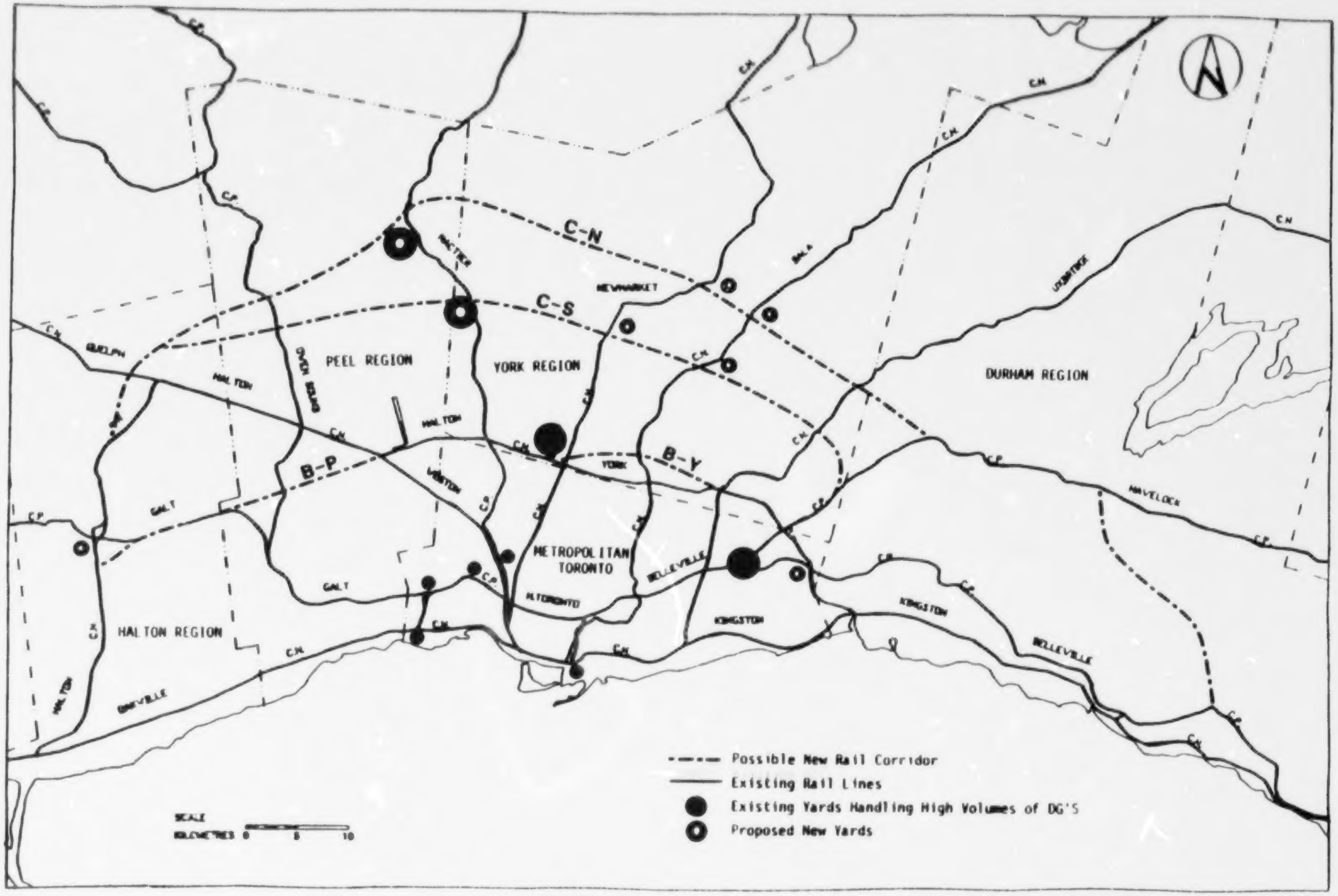
The study area comprises the regional municipalities of Durham, York, Peel, Halton and Metropolitan Toronto, and will be referred to in this study as the Greater Toronto Area (GTA). The existing rail infrastructure and alternative new rail routes are shown in Figure 2. The exhibit also shows the existing yards that experience significant volumes of dangerous goods traffic and the new yards that would be built with some of the alternatives examined.

Meteorology of the Study Area

Meteorological conditions play an important role in the transport and dispersion of clouds of gas or mist that might result from release of some dangerous goods. The frequency of occurrence of various meteorological conditions are therefore required in the assessment of risks due to transport of such materials.

The meteorological data used in the study were obtained from the L.B. Pearson International Airport. The meteorological data from this weather station would be fairly representative of the entire study area in the absence of significant topographical features such as large hills and valleys. The wind pattern may deviate locally in the presence of such features or buildings from that measured at the weather stations. However, the general climatological statistics afforded by the Airport data are sufficient for a risk asses-

FIGURE 2


C-N
C-S
B-Y
B-P
PEEL REGION
YORK REGION
DURHAM REGION
HALTON REGION
METROPOLITAN TORONTO
NEWMARKET
MACTIER
BALA
UXBRIDGE
HAVELOCK
BELLEVILLE
KINGSTON
YORK
WESTON
HALTON
GUELPH
GALT
OAKVILLE
OWEN SOUND
C.N.
C.P.
Possible New Rail Corridor
Existing Rail Lines
Existing Yards Handling High Volumes of DG'S
Proposed New Yards
SCALE
KILOMETRES 0 5 10

sment study of this type which covers a large number of potential release locations in the vicinity of this weather station. The period for which data were analyzed was 1980- 1984.

Hourly values of the meteorological parameters of importance in characterizing dispersion in the atmosphere were then obtained by processing the raw hourly data for this period. The meteorological parameters of importance are:

- Atmospheric Stability
- Wind Speed
- Wind Direction

Atmospheric stability is a measure of the amount of turbulence in the atmosphere. Wind speed governs the rate of airborne DG transport. These two parameters are the most important parameters that influence dispersion. Wind direction is important in that it determines the areas directly affected by an airborne substance. Atmospheric stability for each hour was determined using the methods prescribed in the proposed Ontario Regulation 308 (OME, 1987).

Another meteorological parameter which is of significance in air quality studies but rather unimportant in risk assessments that consider acute hazards only is the mixed layer height. This is due to the fact that dispersion is not usually influenced directly by the mixed layer height until the cloud travels relatively large distances from the release point, and the exposure distances of interest for acute effects are usually smaller than these distances. Therefore, mixing height was not considered as a parameter in this study.

The range of values possible for each meteorological parameter considered in this study is large. In order to simplify the analysis, the hourly values of the meteorological parameters were binned into several categories. A representative value within each category was then selected for analysis purposes. Table 1 shows the categories used for each meteorological parameter and the representative value used for each category.

Calms, which represent conditions of near zero wind speed and therefore have no recorded wind direction, were distributed uniformly into each wind direction and lowest wind speed class.

Atmospheric temperature was assumed to be 20°C. This temperature is typical of summer conditions and overall, is considered to provide conservative estimates of exposure zones. A roughness length of 1 m was used for the entire study region, corresponding to built-up suburban areas.

An analysis of the frequency of occurrence of the various meteorological conditions was then carried out for use in the estimation of risk. The results of this statistical analysis are presented in Table 2. The analysis indicates that winds prevail most frequently from the northwest/west/ southwest with average speeds in the range 3.8 to 4.3 meters per second. This information is presented graphically in Figures 3 and 4 which show wind speed and percentage frequency of occurrence for different wind directions. In terms of stability, the most frequent stability class is neutral.

Traffic Patterns and Operational Strategies

For the existing system, the main DG traffic flows are described below. A more detailed presentation of this information is given by IBI (1987).

The main east-west CP dangerous goods traffic travels along the Galt, North Toronto and Belleville subdivisions (see Figure 2). The north-south traffic travels along the MacTier subdivision. The CP yards that handle the bulk of the DG traffic are the Lambton yard, located at the junction of the Galt, MacTier and North Toronto subdivisions, and the Agincourt yard, located

TABLE 1

Meteorological Data Categories

Meteorological Parameter	Category	Representative Value
Atmospheric Stability	Stable	F
	Neutral	D
	Unstable	B
Wind Speed	< 3 m/s	2 m/s
	3 - 7 m/s	5 m/s
	> 7 m/s	8 m/s
Wind Direction	337.5 - 22.5 deg	North
	22.5 - 67.5	Northeast
	67.5 - 112.5	East
	112.5 - 157.5	Southeast
	157.5 - 202.5	South
	202.5 - 247.5	Southwest
	247.5 - 292.5	West
	292.5 - 337.5	Northwest

Notes: (i) B, D, and F are Pasquill stability classes
(ii) Wind Direction measured clockwise from North

TABLE 2

Meteorological Data Used in the Study
Joint Probability of Occurance of Stability, Wind Speed, and Wind Direction Classes (fraction)*

Stability	Wind Speed	Wind Direction							
		N	NE	E	SE	S	SW	W	NW
Stable	2.0 m/s	3.42E-02	1.53E-02	1.21E-02	2.01E-02	2.50E-02	2.86E-02	4.13E-02	4.40E-02
	5.0 m/s	1.79E-02	2.92E-03	4.14E-03	4.36E-03	4.60E-03	1.03E-02	1.28E-02	1.61E-02
Unstable	2.0 m/s	9.60E-03	5.97E-03	6.68E-03	1.99E-02	1.63E-02	1.01E-02	9.58E-03	8.67E-03
	5.0 m/s	1.10E-02	2.63E-03	5.48E-03	2.04E-02	1.15E-02	9.65E-03	1.31E-02	1.01E-02
	8.0 m/s	1.27E-03	1.50E-04	1.22E-03	7.00E-05	1.70E-04	6.80E-04	1.49E-03	1.83E-03
Neutral	2.0 m/s	1.32E-02	1.01E-02	1.06E-02	1.52E-02	1.54E-02	1.40E-02	1.12E-02	1.08E-02
	5.0 m/s	5.38E-02	1.80E-02	2.66E-02	2.82E-02	1.98E-02	5.05E-02	5.54E-02	5.56E-02
	8.0 m/s	1.57E-02	1.95E-03	9.28E-03	2.68E-03	3.09E-03	2.06E-02	3.16E-02	3.44E-02

* Based on the analysis of 1980-1984 hourly data from L. B. Pearson International Airport.

FIGURE 3 Wind Speed vs Direction

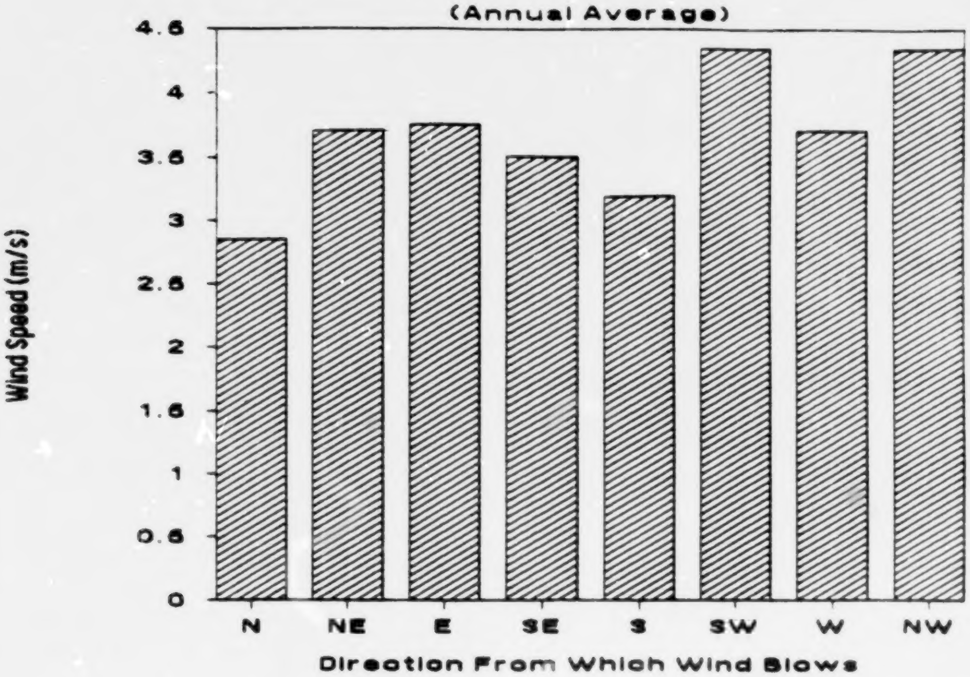
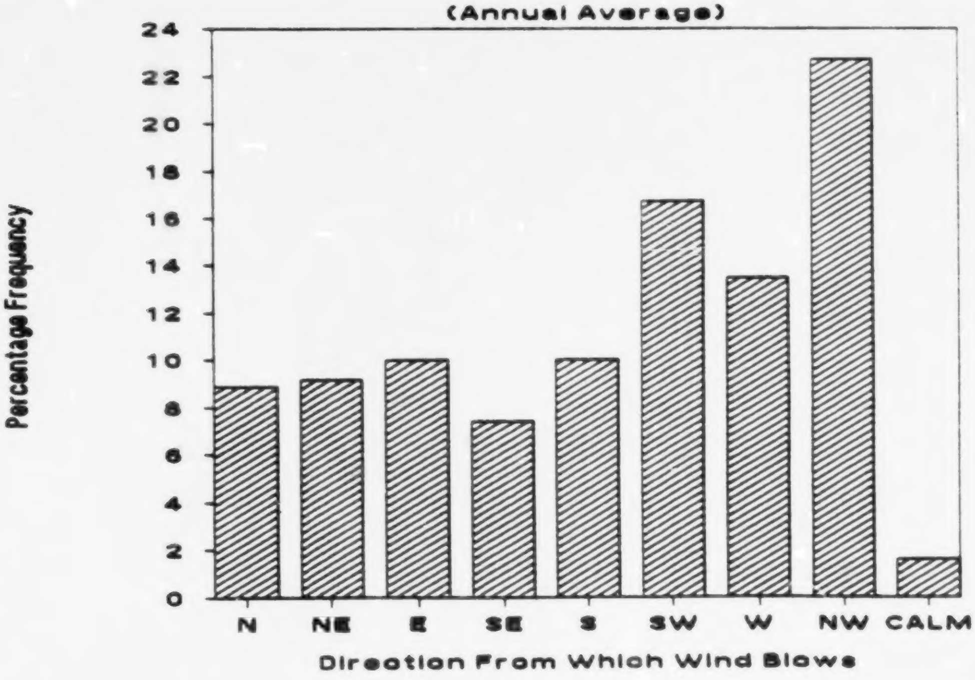


FIGURE 4 Percentage Frequency of Wind vs. Direction



at the junction of the Havelock and Belleville subdivisions. The Agincourt yard is considered CP's main classification yard in the GTA.

The main east-west CN dangerous goods traffic travels along the Halton, York and Kingston subdivisions (the Halton subdivision extends north for some distance in Halton region). The main north-south CN traffic travels along the Bala subdivision. The CN yard that handles the bulk of the DG traffic is the MacMillan yard, CN's main classification yard in the GTA.

A summary of dangerous goods flows is presented in Table 3. Dangerous goods are classified by the railroads into the groups listed below. This classification scheme differs from the classification of dangerous goods as stipulated by the Transportation of Dangerous Goods Regulations (see later)

- Special Dangerous Commodities (SDC's) which include explosive, toxic or corrosive gases and liquids, which could cause significant harm beyond the immediate rail right-of-way.
- Dangerous Commodities (DC's) which include substances which would generally cause harm only within the rail right-of-way.
- Dangerous Mixed Carloads which are generally boxcars containing some packaged goods which could cause a hazardous situation, along with other commodities.
- Residue Cars which are rail tankers that have carried dangerous goods and still contain a residual amount (less than two percent of the car's volume).

It can be seen from Table 3 that 74 percent of the DC traffic and 86 percent of the SDC traffic is through traffic, that is neither originating nor terminating within the GTA. However, only 11 percent of DC mixed loads traffic is through traffic. With respect to residue DG tankcar traffic, it was assumed that the traffic patterns would be the reverse of the full tankcar traffic pattern.

In this study, risk estimates have been made for the years 1991 and 2011. However, traffic patterns have been established from 1985 data. It has been estimated by IBI (1987) that traffic patterns will remain constant up to 2011; that is no growth in the volumes of DG's traffic is anticipated.

Track Characteristics

In order to arrive at estimates of frequencies of occurrence of hazardous events, an engineering assessment of track characteristics for the GTA was required. The data that were felt to be realistically obtainable and which were used for this assessment were:

- switch density data - number of switches per route-mile
- curve data - length of curves, degree of curvature
- rail defects data - rail defects per route-mile
- tie defects data - tie defects per route-mile
- number of level crossings and type of protection
- type of signal control system
- design speed for track
- operating speed for DC's and SDC's

These data were obtained for both the GTA rail network and the Canadian rail network (CN and CP rail networks only). They were used to modify Canadian accident frequencies to reflect the anticipated accident frequencies for the GTA.

For the new routes, not all the required track characteristics data were available; therefore assumptions were made for unknown data.

TABLE 3

Summary of Dangerous Goods Flows*

(Annual Carloads - 1985)
1985 Traffic Composition

	Local	Through	Total	% Through
C.N. TRAFFIC				
Dangerous Mixed Loads	13810	1692	15502	10.9%
D.C. Car loads	3288	6425	9713	66.1%
S.D.C. Car loads	1369	10770	12139	88.7%
All Dangerous Goods	18467	18887	37354	50.6%
Non-dangerous Car loads	280057	271752	551809	49.2%
Residue D.G. Tank Cars	4949	16372	21321	76.8%
Non-dangerous Residue Cars	158428	231465	399893	57.9%
Total Cars	471901	538476	101037	53.3%
C.P. TRAFFIC				
Dangerous Mixed Loads	9312	980	10292	9.5%
D.C. Car loads	2594	9952	12546	79.3%
S.D.C. Car loads	1165	5283	6448	81.9%
All Dangerous Goods	13071	16215	29286	55.4%
Non-dangerous Car loads	235793	185157	421950	44.1%
Residue D.G. Tank Cars	2574	13249	15823	83.7%
Non-dangerous Residue Cars	123150	33326	156476	21.3%
Total Cars	374588	248947	623535	39.9%
TOTAL TRAFFIC				
Dangerous Mixed Loads	23122	2672	25794	10.4%
D.C. Car loads	5882	16377	22259	73.6%
S.D.C. Car loads	2534	16053	18587	86.4%
All Dangerous Goods	31538	35102	66640	52.7%
Non-dangerous Car loads	515850	457909	973759	47.0%
Residue D.G. Tank Cars	7523	29521	37144	79.7%
Non-dangerous Residue Cars	291578	264791	556369	47.6%
Total Cars	846489	787423	1633912	48.2%

* From IBI's Interim Report 3 to the Toronto Area Dangerous Goods Rail Task Force, September 1987.

Rail System Alternatives

The rail system alternatives investigated as part of this risk assessment are shown in Table 4. New rail lines that would be required are shown in Figure 2. The alternatives, which include the existing rail system, or base case, as one alternative (A1), can be divided into three categories:

- Rerouting dangerous traffic through new rail operating strategies (A2)
- Relocating dangerous goods traffic by building new rail lines (B and C alternatives)
- Technology improvements to the rail system as a risk reduction measure (A1T)

Other alternatives, such as speed implications and the establishment of buffers, can also be analyzed using risk assessment methods. However, these were beyond the scope of the present study and therefore not included in the assessment.

The details of the route and operating alternatives are discussed in the report prepared by the IBI Group (1987) in a parallel contract with the Task Force. A brief description is provided below.

Within the "A2" alternative no new rail lines are proposed except some new connections. The main operating change is the diversion of CP dangerous goods through traffic from the Galt, North Toronto and Belleville subdivisions to the CN Halton and York subdivisions.

Within the A1T alternative, several technological improvements have been incorporated. These include implementation of (i) advanced train control, (ii) concrete ties, (iii) converting certain level crossings (depend on train and vehicle densities) to grade separations or improving the crossing protection.

Within the "B" alternatives, new rail lines are proposed. Under alternative B2A, CN would divert dangerous goods through traffic travelling north on the CN Halton subdivision to the CP Galt subdivision. Both CN and CP dangerous goods through traffic travelling along the Galt subdivision would then be diverted to the northeast through the B-P extension (see Figure 2) east of Milton, to rejoin the Halton subdivision and then proceed through the CN York subdivision. Under alternative B2B, a further diversion along the Parkway Belt via new rail line (B-Y) would be implemented.

Under the "C" alternatives, new rail lines would be built to divert all dangerous through traffic to the north of Metropolitan Toronto. Two new routes were considered, a southern route and a northern route (C-S and C-N, respectively).

For each of the alternatives, there are one or more operating alternatives (strategies) examined in terms of risk implications. The various operating strategies include diverting only dangerous goods through traffic or diverting all through freight traffic, and using the existing main classification yards or building new classification yards.

The alternatives for detailed risks were assessed are indicated with a star (*) in Table 4.

Two other alternatives (not shown in Table 4) namely, shifting the CN and CP east-west traffic to either the Lakeshore corridor or the Finch-Hydro corridor, were also investigated, but only in a very approximate manner for scoping purposes. This examination supported an earlier decision not to consider these alternatives in detail since the risk would be higher than the other alternatives, as well as these alternatives not being feasible from an operational or economics point of view.

TABLE 4

Rail System Alternatives

Alternative	Network	CN Traffic Routing	CP Traffic Routing
A1*	Existing	Existing	Existing
A2*	Existing with additional connections	Existing (A1)	Diversion of CP mainline DG trains to Halton/York Subs
B1A	Route B-P (Existing CN York sub)	Milton cut off for all through Halton Sub trains	Route B for mainline DG trains only, Agincourt yard
B1B	Route B-Y (with Thornhill diversion)		
B2A*	Route B-P (existing CN York sub)	Same as B1	Route B for all mainline trains, Agincourt Yard
B2B*	Route B-Y (with Thornhill diversion)		
B3A	Route B-P (existing CN York sub)	Same as B1	Route B for all mainline trains, new Woodbridge Yard
B3B	Route B-Y (with Thornhill diversion)		
C1*	Route C-N (north route)	Route C-N for mainline trains carrying DG's, set-off through DG cars at Vandorf & Cherry to avoid bringing them into MacMillan Yard	Route C-N for all mainline trains, new yard in Bolton area
C2	Route C-N (north route)	Route C-N for all mainline trains, new yard in Vandorf Area	Same as C1
C3*	Route C-S (south route)	Route C-S for mainline trains, carrying DG's, set-off of through DG cars at Elgin and North Maple to avoid bringing them into MacMillan Yard	Route C-S for all mainline trains, new yard in Bolton area
A1T*	Existing with new technology	Existing	Existing

* Indicates the alternatives for which detailed risks were assessed.

RISK ASSESSMENT METHODOLOGY

As mentioned earlier risk is a measure that includes both the consequences of a hazardous release event and its probability of occurrence. Previous studies have attempted to provide some preliminary estimates of risk from dangerous good transport by rail in the Toronto area. These are the studies of Wade (1986) and Burton and Post (1983) which utilized qualitative methods for arriving at risk estimates. In view of the concern over public safety, the present study is a quantitative risk assessment which utilizes the best available data, models and analysis methods and provide greater detail and confidence in the estimates of risk to the public. Application of quantitative risk assessment techniques has become an internationally accepted and integral part of the determination of the safety of the public exposed to majors hazards from industrial operations, such as dangerous goods storage and transportation. The work presented herein constitutes a relatively thorough quantitative risk assessment and as such is a major step forward from previous studies.

Now, to provide an overview of the method used in conducting this risk assessment, refer to Figure 5 where the risk assessment methodology is depicted in simplified form.

The process begins with the identification of hazardous release events. Then, estimates of the consequences and frequencies of the identified hazardous release events are made. These results are then input to the calculation of risk for the rail segments along the routes within a particular rail system alternative. The first set of analyses are done for the existing rail system which is taken as the base case, and as such, risk estimates for this case are considered to be the existing or baseline risk.

The analysis is then repeated for the alternative routes and operating strategies and other risk mitigation measures. Then, the risks associated with alternatives can be examined relative to the existing or baseline risk. This provides a brief overview of the risk assessment methodology. What follows is an explanation of each of the steps discussed above and depicted in Figure 5.

Identification of Hazardous Release Events

In identifying hazardous release events, the first step is examination of the dangerous goods rail traffic. Table 3 provides a summary of dangerous goods flows in the Toronto area for the year 1985, as reported by the IBI Group. These dangerous goods traffic flows were then examined in relation to the system of classification of dangerous goods presented in Table 5. The nine classes presented are regulated by Transport Canada. The first eight classes have been established by the United Nations, and the ninth class is used in Canada and the U.S. A representative substance for each of the most significant classes was then selected for the purposes of the risk analysis work. These substances are also listed in Table 5. The selection was made on the basis of relative hazard and traffic volume. From these considerations, it was possible to identify the hazardous release events for consideration in this study. The three principal hazardous release events are blastwaves, fires, and toxic clouds. These are further described in Table 6 along with the substance which produces the particular hazard. Missiles and tub-rocketing where judged to contribute little to the overall risk and were not directly assessed.

There is a very large variety of hazardous release events with a continuum of consequences. For a risk assessment study of this type, where

FIGURE 5

RISK ASSESSMENT METHODOLOGY

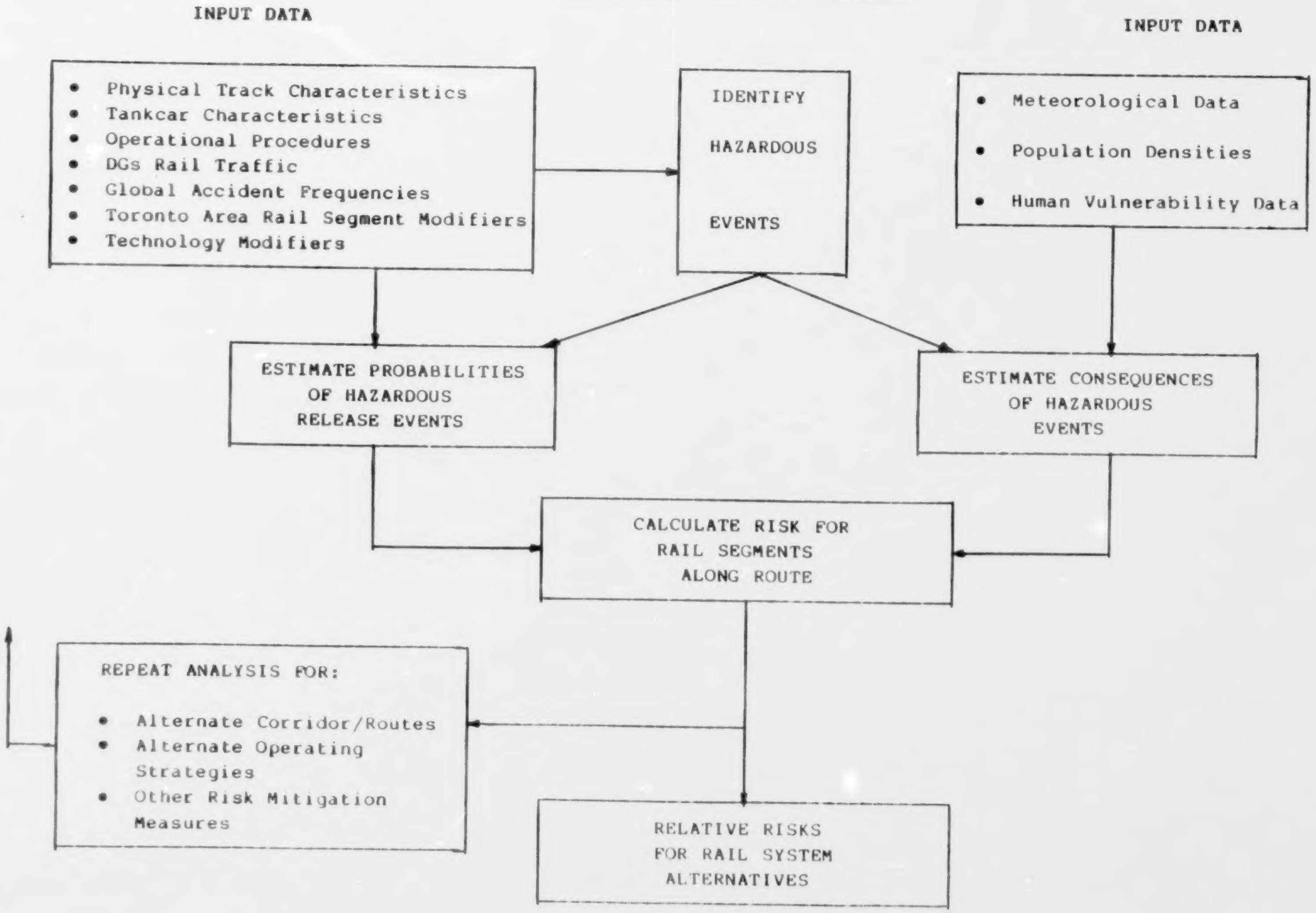

INPUT DATA
• Physical Track Characteristics
• Tankcar Characteristics
• Operational Procedures
• DGs Rail Traffic
• Global Accident Frequencies
• Toronto Area Rail Segment Modifiers
• Technology Modifiers
IDENTIFY HAZARDOUS EVENTS
INPUT DATA
• Meteorological Data
• Population Densities
• Human Vulnerability Data
ESTIMATE PROBABILITIES OF HAZARDOUS RELEASE EVENTS
ESTIMATE CONSEQUENCES OF HAZARDOUS EVENTS
CALCULATE RISK FOR RAIL SEGMENTS ALONG ROUTE
REPEAT ANALYSIS FOR:
• Alternate Corridor/Routes
• Alternate Operating Strategies
• Other Risk Mitigation Measures
RELATIVE RISKS FOR RAIL SYSTEM ALTERNATIVES

TABLE 5

CLASSIFICATION OF DANGEROUS GOODS*

CLASS NO.	CLASS NAME	REPRESENTATIVE SUBSTANCE SELECTED FOR RISK ANALYSIS
1	Explosives	Black Powder
2	Gases - Flammable	Propane
	- Toxic/Corrosive	Chlorine & Ammonia
3	Flammable Liquids	Gasoline
4	Flammable Solids	Phosphorus
5	Oxidizers & Organic Peroxides	Oleum (SO_3)
6	Poisons	
7	Radioactive Materials	-
8	Corrosives	-
9	Miscellaneous Dangerous Goods	-

* Classification of dangerous goods or cargos has occurred at both the national and international level and the above eight classes have been established by the United Nations. The ninth class is used throughout North America.

TABLE 6

HAZARDOUS RELEASE EVENTS

• **BLASTWAVES:**	- due to (i) detonation of explosives, such as **black powder**, (ii) unconfined (flammable) vapour cloud explosions (UVCE's) such as propane, or (iii) boiling liquid expandinding vapour explosions (BLEVE's), such as propane
• **FIRES:**	- pool fires from pools of flammable materials such as **gasoline** - jet fires from release of flammable materials, such as **propane**, from pressurized vessels - fireballs from boiling liquid expanding vapour explosions (BLEVE's) of pressure-liquefied flammable gases such as **propane** - flammable clouds from release of flammable substances such as **propane**.
• **TOXIC GAS CLOUDS:**	- from release of toxic substances such as **chlorine, ammonia or oleum** or from the combustion products from burning of substances such as **phosphorus**.

the emphasis is to provide estimates of relative risks of various alternatives for the purpose of making risk management decisions, it is not necessary to examine each and every possible hazardous release event in detail. It is sufficient to group these events and identify a representative release event for that group, in a manner consistent with the approach of selecting representative chemicals for the different groups of dangerous goods transported in the Toronto Area as described above. To this end, release events that could lead to similar consequences were grouped together, and surrogate events were selected for each group which would represent the consequences of the events in their respective groups. The types of events used in this study are large release rate (LRR) or small release rate (SRR) events, taking place with or without the presence of external fires (WF or NF, respectively).

Consequences of Hazardous Release Events

Estimating the consequences of hazardous release events requires first a determination of the area or zone around the accident where the effects of blastwaves, fires, or gas clouds would have harmful impacts on people. Next, a determination must be made of the number of people who could be within that zone. Clearly then, the consequences of a hazard are dependent on location, and the greater the population density, the greater the potential consequences.

To make the estimates of consequences requires the use of mathematical models which estimate the size of the hazard zone due to blastwaves, fires and toxic gas clouds. The models which have been used are state-of-the-art models which require as input meteorological data, population densities, human vulnerability data and release characteristics. Meteorological data consist of the frequency of occurrence of different meteorological conditions (e.g., windspeed, wind direction and atmospheric stability) determined from a statistical analysis of five years of data (1980-1984) from the Lester B. Pearson International Airport, which is taken as representative for the Toronto study area.

The population densities used in this study were obtained from the Ontario Ministry of Transport and Communications (MTC) projections for the years 1991 and 2011 (Toronto Regional Modelling System - TARMS - data). The human vulnerability data were taken from the published literature on effects on humans (e.g., the toxic effect of chemicals on humans). The consequence models used in this study take into account the time varying nature of accidental releases, the exposure time, the human dose/response relationships, and the variability in human vulnerability.

Frequencies of Hazardous Release Events

The probability of occurrence of a hazardous release event is estimated based upon historical accident data and using techniques such as fault and event tree analyses.

The base accident frequencies (initiating faults) were obtained by an examination of CTC Accident Records for the six year period 1980-1985 for CN and CP. Each accident was classified as to its reported base accident cause. By employing appropriate Canada-wide divisors (e.g., number of train miles travelled per year) for each accident cause, the base accident frequencies were estimated (e.g., number of broken wheels per car-mile). The base frequencies were modified using appropriate modifiers to reflect the local traffic and track characteristics specific to a given segment in the Toronto rail system. The physical track characteristics were defined in terms of location and quality of main line track segments, switching segments, and marshalling yards. The modified base frequencies for the Toronto area were then used as inputs to fault and event trees for each chemical.

The results of this analysis lead to the expected frequencies (or likelihood) of hazardous release events.

Risk Calculations

Once the probabilities and consequences of hazardous release events are estimated, quantitative estimates of risk are then possible. The risk for a particular hazard is calculated by multiplying the frequency of occurrence of the hazardous release event by the consequences of this event. The risk due to a complete facility, such as the entire rail system in the Toronto area, can be obtained by summing together all of the risk estimates for all of the possible hazardous release events for all rail segments in the system.

As an example, if the expected frequency of occurrence of a small propane release resulting in a jet fire due to derailment on a specific rail segment is 1 event in 10,000 years and the expected consequence is 50 fatalities for this event, then the risk due to this hazard is expressed as:

$$\text{Risk} = \text{Hazard Frequency} \times \text{Hazard Consequence}$$

$$= \frac{1 \text{ event}}{10{,}000 \text{ years}} \times \frac{50 \text{ fatalities}}{\text{event}}$$

$$= 1 \text{ fatality in } 200 \text{ years due to this hazard.}$$

The risk parameter calculated above is the societal risk for the area around the specific rail segment due to this particular hazard.

For the purposes of estimating individual risk, calculations similar to the above are used except that population densities are not taken into consideration. The resulting estimate of individual risk is then a measure of the chance of a person living at a particular distance from the rail line becoming a fatality. As would be expected, individual risk decreases with increasing distance from the rail line.

In this study, both individual risk and societal risk are estimated. The above calculation procedures were first carried out for all rail segments along all routes in the existing rail system (base case). The baseline societal risk is then determined by summing the societal risk estimates for all segments within the system. Refering back to Figure 5, once the risk estimates for the existing system were made, the analysis was then carried out for the alternative routes/corridors and operating strategies as well as for other risk mitigation measures. The alternatives for which detailed risk estimates were made were identified in Table 4. With these analyses completed, the relative risks for the rail system alternatives were examined to determine which alternatives or measures lead to the greatest reduction in societal risk.

DISCUSSION OF RESULTS

Societal Risk for Rail System Alternatives

We shall now present some of the key risk results of the study and put them in perspective by providing comparisons with other more familiar risks.

The key parameter of importance in this study is the system societal risk which would give an indication of the relative merits of the alternative rail systems examined in this study in terms of risk to the public. The system societal risk estimates for the base case (Alternative A1) and 1991 population densities is about 4.1 fatalities per year for the entire Greater Toronto Area (GTA). This can be compared with societal risks due to some other hazardous events (see Table 7). For example, fatalities due to smoking per 100,000 smokers is 300 per year (not in the table), and fatalities in Canada due to poisoning is about 700 per year. These comparisons with other common risks provide only one way of putting the risk estimates from this study into perspective. The societal risk due to rail transportation of dangerous goods in the Toronto Area is lower than all the other risks in the table except perhaps cataclysmic storms, earth movements and lightning (if, for example, for cataclysmic storms a comparison is made by prorating the Canada-wide number of 13 to the Toronto Area with a population of let's say 1/10th of Canada, the societal risk would be about 1.3 fatalities per year due to storms in the Toronto Area; this is about a third that due to rail TDG risk).

Societal risk comparisons similar to those made in Table 7 are frequently used in risk assessments. However, when making such comparisons, one ought to be cautious. Although the comparisons made provide some value, a more meaningful comparison could be made with a proper basis of comparison - the exposed populations for each activity. Societal risk values can then be expressed in terms of deaths per year per number of exposed persons (e.g. one thousand). This extension in comparison was not carried through in this study because exposed populations for the common activities shown in Table 7 were not readily available. The entire Canadian population can be used in several, but not all cases, since phenomena such as earth movements would not affect the entire population.

One must make another distinction between the rail TDG risks as estimated in this study and the others in Table 7. The rail risk estimates are in terms of what is usually termed as "statistical fatalites;" they are not the actual expected number of fatalities in any given year. The average annual risk given in "statistical fatalities per year" reflect the likelihood that there might not be any such deaths over an extended period of years but there is always the possibility of an accident which could cause multiple deaths, thereby bringing the average upto the societal risk number given above.

Another way of comparing risks due to various hazardous activities or events is to compare their risk spectra on one graph. Risk spectra are curves which present a more detailed picture of the frequency and consequence of the individual events that make up the hazardous activity. An example is shown in Figure 6. Here, the ordinate is the frequency of events having a consequence of N fatalities or more, and the abscissa is the number of fatalities N. In the figure, the risk spectrum for the existing rail system is shown together with the curves for various other hazards as given in the Reactor Safety Study published by the U.S. Nuclear Regulatory Commisssion in 1975. As can be seen, the rail TDG risks in the Toronto Area are again relatively small compared to these hazards.

Another factor that must be kept in mind in the interpretation of the risk estimates of this study is the uncertainties in these estimates. In general, these uncertainties are of three types:

- Bias introduced in the selection of, for example, the representative chemicals or release events for their respective groupings. The

TABLE 7

Societal Risk
Due to Various Hazardous Events

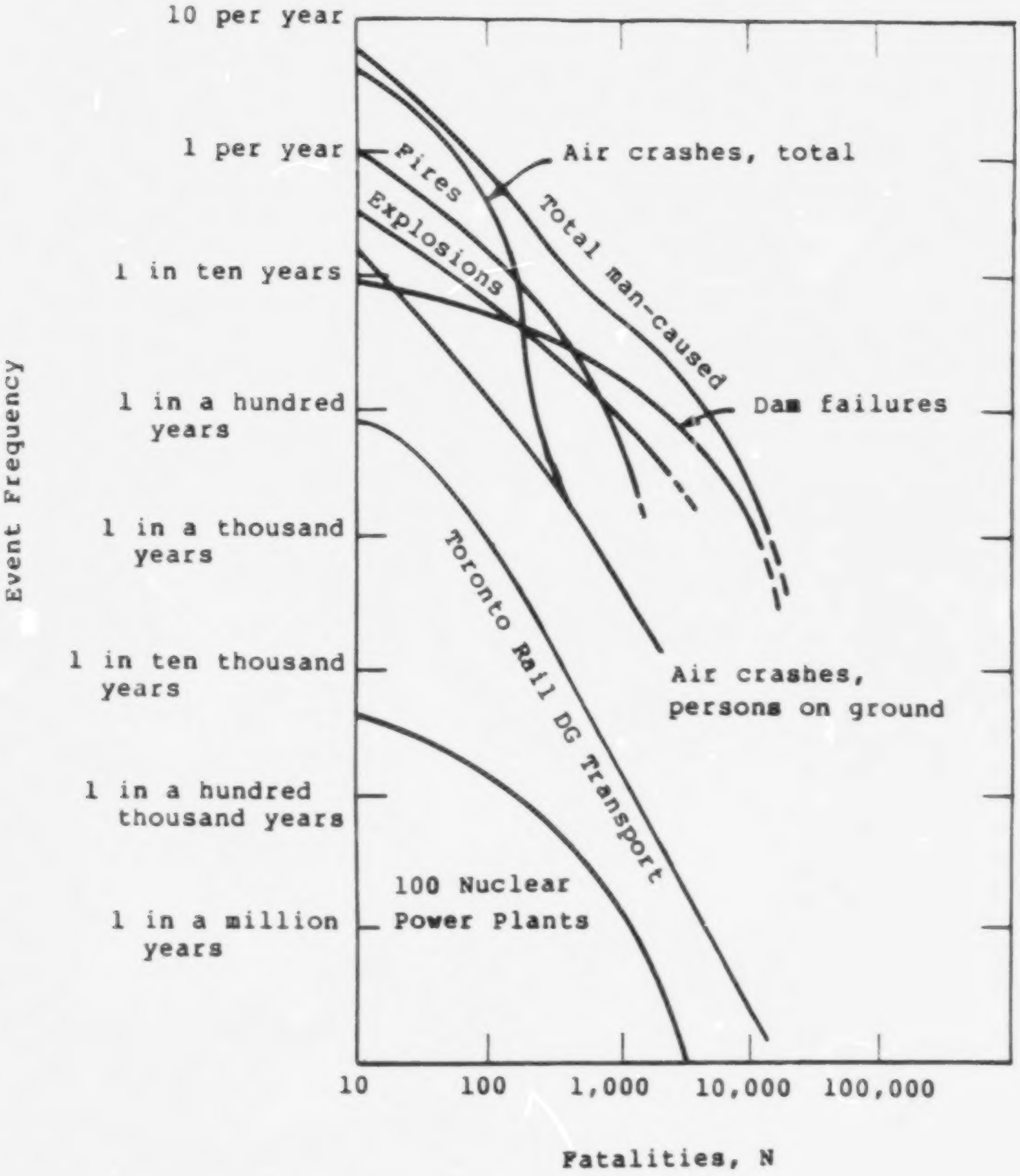
	Societal Risk (fatalities per year)
Motor vehicle accidents	4,238
Falls	1,829
Poisoning+	665
Dwelling Fires	487
Excessive cold	121
Cataclysmic storms	13
Earth movements	5
Lightning	3
Rail Transport of Dangerous Goods (TDG) in the Greater Toronto Area (baseline risk based on existing system)	4.1*

*This is the estimated societal risk in "statistical" fatalities per year as determined by risk assessment. All of the other societal risk numbers are "actual" fatalities recorded Canada-wide. (Source: Statistics Canada, 1985, "Causes of Death," Publication #84203.)

+Includes accidental poisoning due to poisonous and other substances, surgical complications and misadventures to patients.

FIGURE 6

Societal Risk for the Existing System Expressed in Terms of Frequency of Events with Consequences Equal to or Greater Than a Given Number of Fatalities Versus Number of Fatalities (Adapted from Reactor Safety Study, WASH-1400, NRC, 1975)



bias introduced here is on the conservative side, i.e., it will lead to higher estimates of risk than actual.

- Uncertainties due to errors in input data, such as accident frequencies, population data, meteorological data, etc. These errors would normally be random and not introduce any systematic bias in the risk estimates.
- Uncertainties due to model simplifications and assumptions in the consequence models or in the rail system model used in estimating event frequencies. The model assumptions are in general made such that the model results would "err on the safe side", i.e., lead to higher estimates of risks than actual.

The overall results of introducing these uncertainties are expected to be conservative risk estimates.

It is difficult to define the magnitude of these uncertainties without extensive sensitivity and error propagation analyses. However, a rough estimate can be provided based on professional judgement: the overall system societal risk would likely be between a high of two times and a low of one-tenth of the estimate given, and probably closer to about one-third of the estimate. It should be noted, that these uncertainties would be of particular importance when absolute risks are required. When relative risks are being addressed, as in the present study, comparisons between various alternatives can be made with a lot more confidence than the above uncertainties might indicate, because the risk estimates for each alternative would have uncertainties in the same direction (e.g., risk estimates would be high) by about the same magnitude.

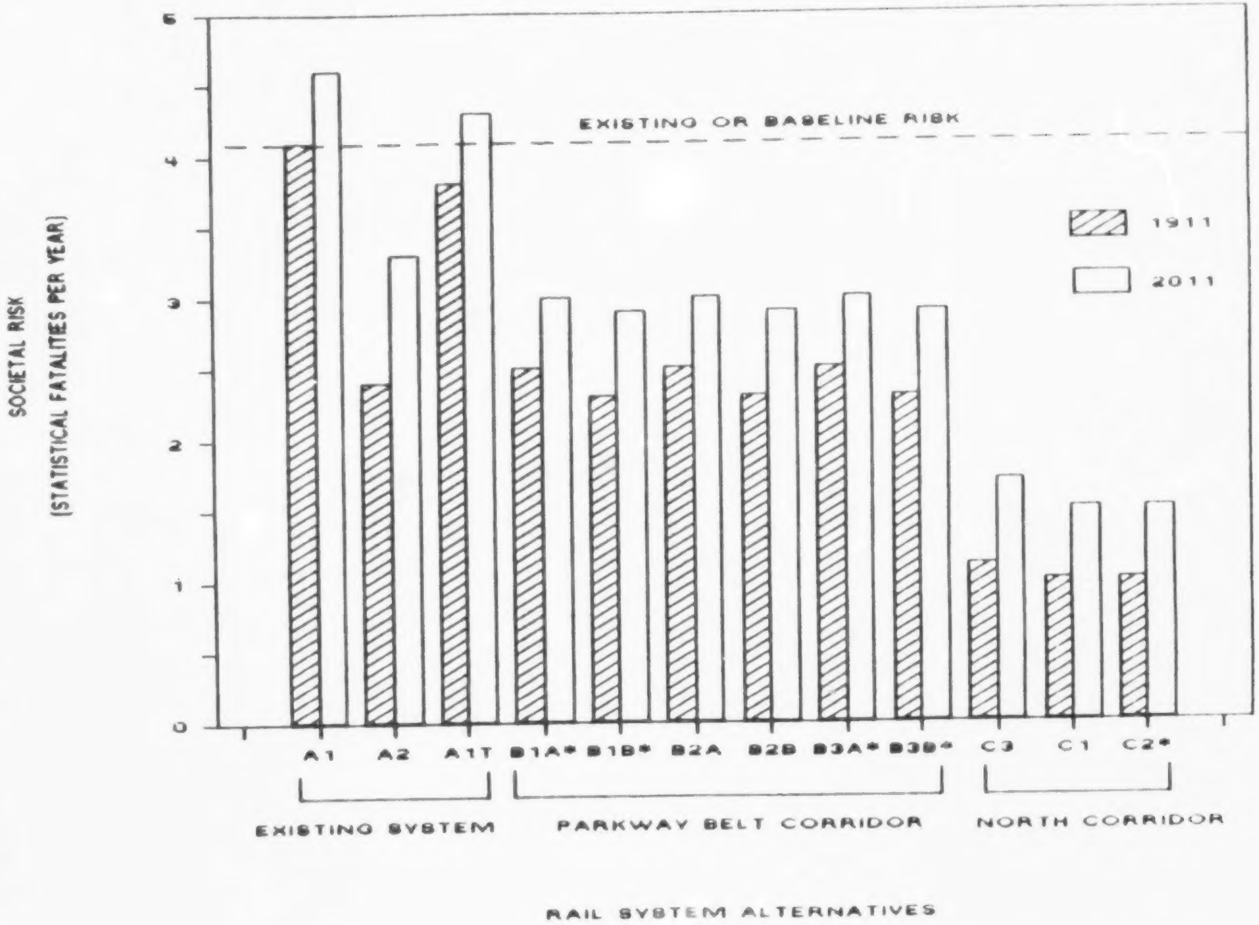
With this perspective in mind, let us now examine the system societal risk estimates for the various alternatives presented in Figure 7. Let us first compare the year 1991 with 2011. The differences here are strictly due to population changes. For all the alternatives, the estimated societal risk increases for the year 2011. This is an expected result since population is expected to increase from 1991 to 2011. The relative increases from one alternative to another are quite different, however, the percentage increase for the existing system (A1, (4.6-4.1)/4.1 = 12%) being much less than the percentage increase, for example, for alternative C1 (Route C - North). This is also as expected since population growth is projected to be much faster in the outlying areas than within the presently built-up areas.

Alternatives A2 and B2 (both B2A and B2B) represent significant societal risk reductions over the base case A1. The main reason for this is the obvious one: CP dangerous goods traffic is diverted away from the more densely populated regions to less densely populated regions. However, there is practically no difference between A2 and B2 (1991), indicating that diversion of both CN and CP dangerous goods traffic from the present CN Halton Subdivision near the Georgetown area south to the Milton cut-off produces a negligible net effect for 1991 even though the Milton cut-off route is shorter. For 2011, the projected higher population growth along the CN Halton Subdivision leads to higher societal risk estimates for A2 than for B2.

Alternatives C1 (northern route) and C3 (southern route) also represent significant reductions in system societal risk, with respect to both the A and B alternatives, mainly again due to much lower population densities, in spite of the much longer rail travel distances. The difference between C1 and C3 is not as much as would be expected due to this compensating effect.

FIGURE 7

COMPARISON OF SOCIETAL RISKS FOR RAIL SYSTEM ALTERNATIVES



*INFERRED THROUGH EXAMINATION OF RESULTS FOR THE ALTERNATIVES FOR WHICH DETAILED RISKS WERE ASSESSED.

The technology improvements (A1T), as proposed for application to the existing system, result in less than 10% reduction in the system societal risk.

In Figure 7, the societal risk figures indicated with * were inferred through examination of results for the alternatives for which detailed risks were assessed. These results indicate that the alternatives B1 and B3 are expected to result in risks similar to B2; and alternative C2 would probably result in risks similar to C1.

One of the main reasons that the societal risk does not drop further than shown relative to A1 especially for the C alternatives is that a considerable amount of local DG traffic must remain in the densely populated areas, to service the industries located in these areas. If the traffic patterns change for reasons such as re-location of industries, the estimated 2011 societal risk might well be reduced from the 1991 level.

A striking observation that can be made from Figure 6 is that there are essentially three principal levels of societal risk for the alternatives examined: the baseline risk, the risk level achieved by diversion of CP North Toronto DG traffic to the CN Halton and York Subdivisions or the Parkway Belt (A2 or B alternatives), and the risk level achieved by diversion of all DG traffic to the north corridor (C alternatives). The risk reduction from the existing level for Alternatives A2 through B3B is roughly 40% and for C1 through C3 about 75%. The increase in risk from 1991 to 2011 goes from a minimum of 12% for A1 to a maximum of 50% for C3 which is expected since the population is anticipated to grow much more rapidly in the north corridor areas. Now, to examine how particular segments are being affected and by how much, one must look at the societal risk distribution in the study area, which is discussed in the next section.

Societal Risk Distribution in the Toronto Area

The rail system societal risk comprises the societal risk estimates for the individual rail segments which make up the system. To give an example of the distribution of the rail TDG risks in the Toronto Area, the societal risk estimates for each segment in the existing system (A1) are presented in detail in Table 8. Here, the segment societal risk in terms of fatalities per year due to rail operations on that segment is given for the subdivisions (and yards) as listed. For risk assessment purposes some of the subdivisions have been further divided into rail segments of uniform accident environment. Also shown in Table 8 is the societal risk rate along each segment in terms of fatalities/ (year•km).

Although the segment societal risk is more useful when comparing one alternative to the other (the sum of the segment societal risks gives the system societal risk), the societal risk rate along each segment is more meaningful when comparing one segment with another. Hence, this last parameter is presented graphically on the map in Figure 8 for the existing system (1991 population). A key to this figure is given on the page following the map. The CP North Toronto and CN York (Thornhill area) Subdivisions have higher societal risk rates than the other subdivisions in the Toronto Area.

By examining similar maps for each of the alternatives, one can identify which areas would experience higher or lower risks relative to the base case and each other.

Individual Risk Near Rail Lines

Individual risk is a measure of the chance of a person who is at a particular distance from the rail line becoming a fatality due to TDG

TABLE 8

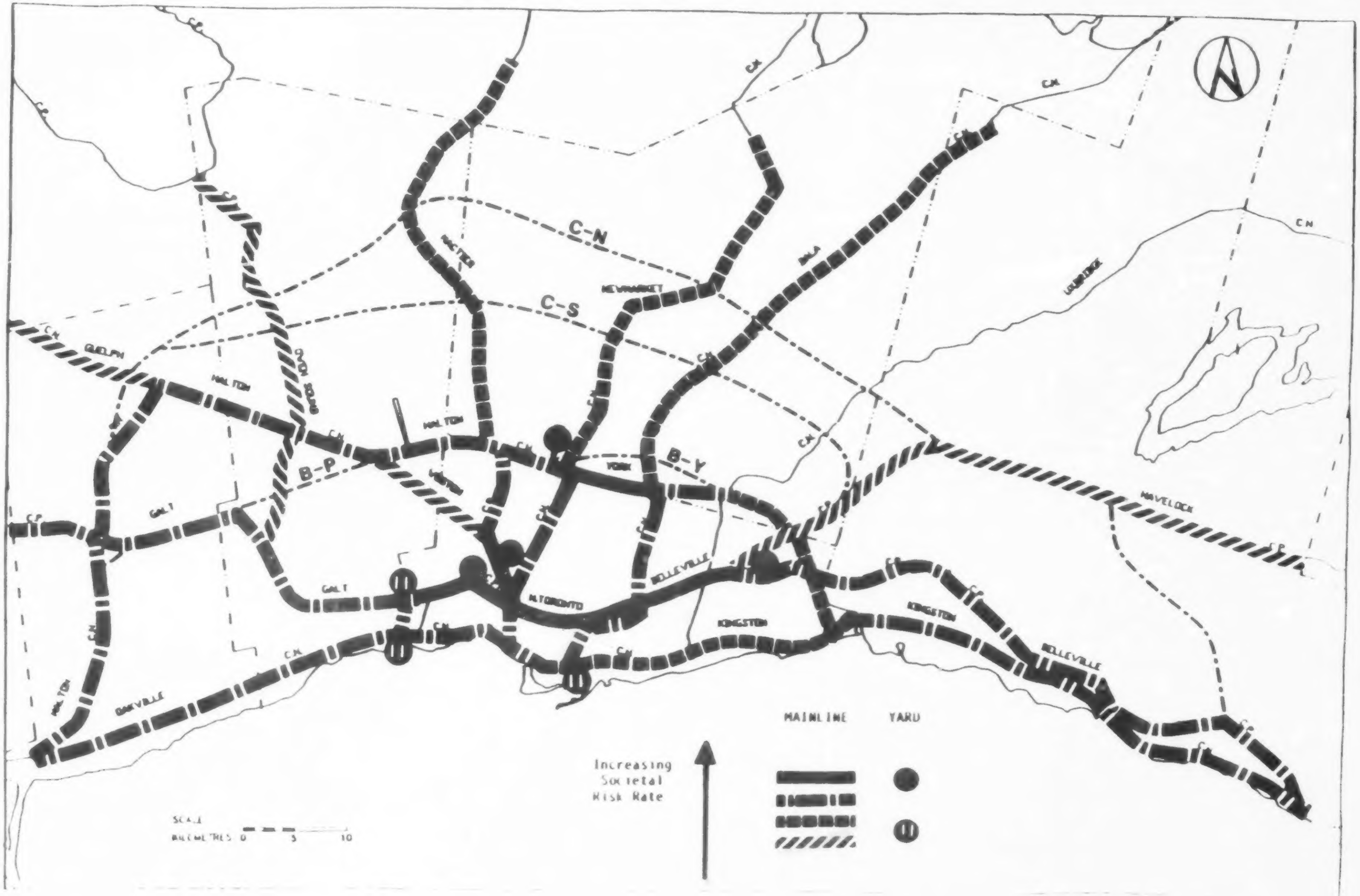
SYSTEM RISK TABLE : Alternative A1 for 1991

Segment	Subdivision	Length (km)	Societal Risk For Segment (Fatalities/ Year)	Societal Risk Rate Along Segment (Fatalities/ Year-km)
A1-01	CP Galt	15.6	0.0464	0.0030
A1-02	CP Galt	34.5	0.1707	0.0049
A1-03	CP Galt	2.4	0.0300	0.0125
A1-04	CP Galt	3.9	0.0675	0.0173
A1-05	CP Galt\N. Toronto	3.0	0.2341	0.0780
A1-06	CP N. Toronto	9.1	0.3642	0.0400
A1-07	CP Belleville	12.5	0.1793	0.0143
A1-08	CP Belleville	4.6	0.0259	0.0056
A1-09	CP Belleville	64.3	0.1026	0.0016
A1-10	CN Oakville	38.0	0.1180	0.0031
A1-11	CP Canpa	4.2	0.0110	0.0026
A1-12	CN Oakville	13.4	0.0201	0.0015
A1-13	CN Weston	9.4	0.0004	0.000043
A1-14	CN Weston	5.7	0.0282	0.0049
A1-15	CN Kingston	32.6	0.0055	0.00017
A1-16	CP Havelock	42.8	0.0007	0.000017
A1-17	CN Halton	65.6	0.3848	0.0059
A1-18	CN Halton	7.6	0.0646	0.0085
A1-19	CN Halton\York	9.0	0.0208	0.0023
A1-20	CN York	7.3	0.1947	0.0267
A1-21	CN York	8.0	0.0435	0.0054
A1-22	CN York	23.4	0.0050	0.00021
A1-23	CN Kingston	52.5	0.1061	0.0020
A1-24	CP MacTier	16.4	0.0060	0.00036
A1-25	CP MacTier	17.8	0.0095	0.00053
A1-26	CP MacTier	9.2	0.0179	0.0020
A1-27	CP MacTier\CN Weston	7.1	0.1448	0.0204
A1-28	CN Newmarket	44.6	0.0131	0.00029
A1-29	CN Newmarket	14.2	0.0589	0.0041
A1-30	CN Bala	21.3	0.0141	0.00066
A1-31	CN Bala	62.0	0.0462	0.00075
A1-32	CN Bala	22.9	0.0589	0.0026
A1-33	CP Owen Sound	57.9	0.0001	0.000003
A1-34	CN Guelph	13.5	0.0005	0.000037
	Yards			
A1-Y1	CN MacMillan		0.6776	
A1-Y2	CN Mimico		0.0015	
A1-Y3	CN Don		0.0059	
A1-Y4	CP Agincourt		0.0931	
A1-Y5	CP Lambton		0.6068	
A1-Y6	CP Obico		0.0045	
A1-Y7	CP Ray Ave		0.0917	

Total Societal Risk for Toronto Area Rail System
= Sum of Societal Risks for all Segments = 4.1 Fatalities/Year

FIGURE 8

Societal Risk Distribution in the Toronto Area for DG Rail Transport Routes in the Existing System


C-N
C-S
B-P
B-Y
CN
CP
GUELPH
HALTON
OWEN SOUND
MACTIER
NEWMARKET
BALA
UXBRIDGE
YORK
GALT
TORONTO
BELLEVILLE
KINGSTON
HAVELOCK
OAKVILLE
MAINLINE
YARD
Increasing Societal Risk Rate
SCALE
KILOMETRES 0 5 10

KEY TO RELATIVE SOCIETAL RISK RATE MAP

RAIL LINE SEGMENTS

Estimated Risk Range in Fatalities per km per year	Map Key	Estimated Risk Range In Fatalities per km
$10x10^{-3} < R < 100x10^{-3}$	▬	1 every 10 to 100 yrs.
$1x10^{-3} < R < 10x10^{-3}$	▮▬▮	1 every 100 to 1,000 yrs.
$0.1x10^{-3} < R < 1x10^{-3}$	■■■■	1 every 1000 to 10,000 yrs.
$R < 0.1x10^{-3}$	▨	less than 1 every 10,000 yrs.

YARDS

Estimated Risk Range in Fatalities per year		Estimated Risk Range In Fatalities
$10x10^{-3} < R < 800 x 10^{-3}$	●	1 every 1 1/4 to 100 yrs.
$R < 10 x 10^{-3}$	◍	less than 1 every 100 yrs.

accidents on that rail line. This risk decreases with increasing distance from the rail line since the potential for the hazards to cause impacts decreases with increasing distance from the rail line. The individual risk profiles near a high-traffic rail segment in the Toronto Area are shown in Figure 9. Also shown are individual risk numbers for the other hazards that were considered earlier for comparative purposes.

As a sample interpretation of this figure, if a person lived about 1.2 km north of the rail line, the risk of being killed as a result of a DG accident is about the same as the risk of being struck and killed by lightning (i.e., about 1 chance in 8 million annually). It should be noted here that all of these risks except that due to smoking and being in a motor vehicle can be considered to be involuntary risks. There is generally less public acceptance of involuntary risks than of voluntary risks such as smoking. The one in a million level, which is generally considered to be an acceptable level for individual risks of an involuntary nature, is reached at about 400 m from the rail line. Before making any judgements as to the acceptability of the risks near a rail line, however, the uncertainties in the risk estimates must be considered in some detail since for such judgements one must be concerned more about absolute risk than relative risk which has been the focus of the present study.

Summary

This paper has briefly described the approach and results of the assessment of risk to the public for the possible rail system alternatives relative to the baseline risk for the existing system. The full details of this work are documented in the major report on this study.

The study constitutes the most comprehensive of its kind to date for assessing risks due to dangerous goods rail transport in the Greater Toronto Area. It has utilized state-of-the-art consequence and frequency assessment models covering the full range of possible hazards due to DG transport. It has drawn upon a large and comprehensive volume of data, such as:

- DG traffic pattern and operational strategies in the GTA,
- population densities adjacent to rail lines within the GTA,
- meteorological data fro the GTA,
- track information (fixed plant) both within the GTA and Canada-wide,
- equipment information (e.g., tankcar design),
- historical accident data (Canada-wide),
- human vulnerability data.

Throughout the study, focus was on quantitative estimates of risk as opposed to qualitative aspects, which were the subject of all the earlier studies on risk assessments for DG rail transport in the study area.

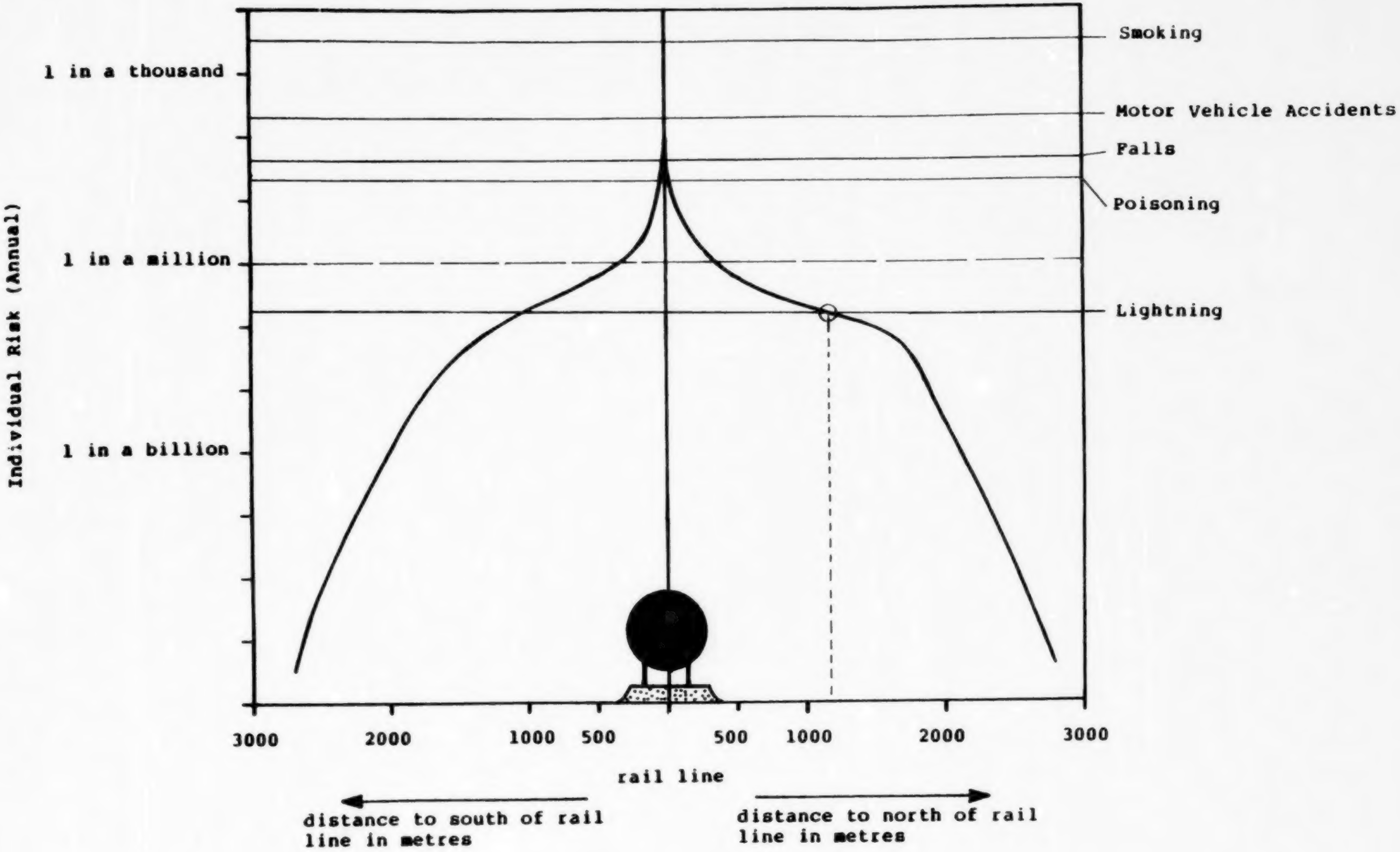
The results of this study indicate that the baseline societal risk for the existing rail system is 4.1 statistical fatalities per year based upon 1991 population data and 4.6 for the year 2011. These levels of public risk are relatively low when compared to other societal risks.

If these levels of societal risk are considered unacceptable, significant reductions in public risk are afforded by the various alternatives investigated.

While it is anticipated that the estimated levels of societal risk for the present system will be examined with a view to assessing the acceptability of these levels, it is important to bear in mind the uncertainties associated with the estimates.

FIGURE 9

Individual Risk - Chance of an Individual near a rail line becoming a fatality (high rail traffic segment in GTA, 1991)



Even though the above considerations, which focus on the risk estimates in an absolute sense, are unavoidable, it must be stressed that the principal thrust of this work is on the relative risk to the public from possible alternatives to the current rail system. The results of this study which are based upon a quantitative assessment of the risks provide valuable guidance on which alternatives produce the most significant measure of risk reduction.

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ENVIRONMENTAL AUDITS MAY PREVENT SPILLS OF HAZARDOUS MATERIALS

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1.0 INTRODUCTION

Early in 1987 a project was initiated to first contain and then cleanup PCBs that were spilled in the cold draw area of a plant. The project developed along parallel paths to first contain and cleanup the PCBs that were spread around the north-east end of the Cold Draw Department when about 20 L of a 1% PCB oils were spilled on Railcar 1521. The second part of the project was to decontaminate the HS area within the Cold Draw Department which, as later testing showed, was heavily contaminated with PCBs. This report summarizes the details of the decontamination project.

2.0 SUMMARY

The HS area in the Cold Draw Department was commissioned in 1950 to swage or taper one end of the pipe. The process equipment included a furnace, a swager itself, a push bench, a hydraulic power pack, and the associated pipe handling equipment.

The process operates at a high temperature and, as a result, hydraulic oil in the push bench system was specified for high temperature operation. In 1950 Pydraul A312 was employed in the unit which contained PCB for resistance to the high temperatures. The use of Pydraul A312 was discontinued early in 1970 when the supplier replaced Pydraul A312 with 312C. It was only recently discovered by management that A312 contained PCBs. Since then the hydraulic oil had been changed during normal maintenance on the equipment.

A decision was made to discontinue the use of the swager and to replace it with a cold pointer. Therefore decommissioning of the equipment was begun. Management staff was in the process of analyzing various oils for PCB when a sample of oil from the hydraulic unit was taken and sent to a lab for analysis for PCB. While awaiting for analysis, on the belief by supervision that the risks were minimal, decommissioning was continued. This consisted of disassembling equipment in the HS area and moving it by overhead crane to flat bed railcars on the cold draw spur on the other side of the plant.

On day 1, the hydraulic unit, which consisted of the oil reservoir, the pump and the motor, was moved from the HS area to Railcar 1521. The unit had not been drained and still contained about 20 L of oil. It was standard practice at the plant to leave oil in equipment when it was being decommissioned. Normally old equipment was stored in various parts of the plant for a period of about 10 years in the event it might be usable at a later date. Oil was normally left in gear boxes, hydraulic units etc., to prevent rusting.

On day 2 someone noticed that the hydraulic unit had tipped over on Railcar 1521. Oil spilled onto the deck of the car and ran down onto the floor and tracks below. An absorbent material was spread on the oil on the floor and on the railcar. Railcar 1521 was then shunted out of the Cold Draw Department and parked on a siding. Some oil continued to drip off the car as it was moved. Portions of the track and bed were contaminated with oil.

On day 2 at 10:00 a.m., management learned from the lab that the oil from the hydraulic drive unit contained 10,000 ppm of PCB even after 15 years of continuous service and routine maintenance. Decommissioning work in the HS area was terminated immediately. The cleanup operation began that afternoon. Subsequent testing showed that, while the majority of the equipment was not contaminated with PCBs, some had surface concentrations of 5,000 micrograms per square metre or more.

The cleanup of the spilled oil in the north-east section of the Cold Draw Department proceeded smoothly. Normal operations in that area of plant were restored within 4 days, however the cleanup of the entire area which had been involved with the spill and the decontamination of the HS area was not completed until day 60 or 2 months after the initial spill.

3.0 CONCLUSION

The price that had to be payed for not knowing that a hazardous chemical was present in the plant cannot simply be measured by the strict cost of labour and materials to cleanup the spill. The project cost must include the effect of having the spill on

a) relationships among all staff at the plant,

b) the reputation of the company in the community and with government agencies,

c) lost production from various causes.

The total cost is difficult to access in dollars. The strict cost of cleaning up the spill of 160 grams of PCBs in 16 kilograms of oil was $75,000. To have the knowledge of the presence of a hazardous chemical in your plant may cost you some money, however you will save money in the long run by avoiding unexpected crisis similar to the one described here. A simple cleanup job that should have cost $40,000 turned into a $115,000 project because of the spill.

An environmental audit could have avoided this costly error.